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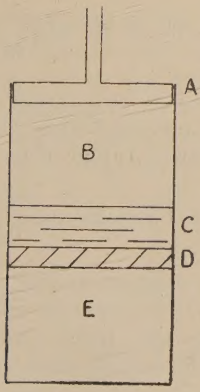
XLVIII. *The Effect of the Presence of an "Indifferent" Gas on the Concentration and Activity of a Vapour in Equilibrium with a Condensed Phase or System of Condensed Phases.* By IVAN ROY MCHAFFIE *.

Introductory.

THE effect of the presence of an indifferent gas on the concentration and activity of a vapour in equilibrium with a condensed (solid or liquid) phase may be expressed quantitatively in the following manner. The concentration of the indifferent gas may be increased by increasing its

Fig. 1.



pressure in a vapour chamber in contact with the condensed phase according to the system shown in fig. 1. A represents a piston exerting a pressure P ; B a chamber containing the

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indifferent gas and vapour from C; C the solid (or liquid) system; D a fixed semipermeable membrane permeable only to the vapour of C; E a chamber containing only this vapour. It is assumed that, at the chosen temperature T, the pressure of vapour in E is small. It will also be small in B. It is also assumed that the effect of the solubility of the indifferent gas in C may be neglected, and that C is a pure solid (or liquid) substance S.

If F_S be the molar free energy * of the solid (or liquid) S at the temperature T and the pressure P; F the corresponding molar free energy of S vapour in E; and $\bar{F}$ the partial molar free energy of S vapour in B, then, when equilibrium is reached,

$$\bar{F} = F_S = F.$$

For a change in total pressure, the temperature remaining constant,

$$\left(\frac{\partial \bar{F}}{\partial P}\right)_T = \left(\frac{\partial F}{\partial P}\right)_T = \left(\frac{\partial F_S}{\partial P}\right)_T = V_S, \quad . \quad . \quad . \quad . \quad (1)$$

where V_S is the molar volume of the solid (or liquid) substance S. It is supposed in the present case that the increase of pressure is caused by an increase in the concentration (and partial pressure) of the indifferent gas.

Let F_0 be the molar free energy of S vapour in some standard state. If in all states S vapour follows ideal gas behaviour, then, for an isothermal process,

$$\bar{F} - F_0 = RT \log \frac{c}{c_0},$$

where c and c_0 are the concentrations in the corresponding states. If S vapour does not follow the ideal gas behaviour, the above equation may be replaced by the (partial) definition equation,

$$\bar{F} - F_0 = RT \log \frac{a'}{a_0'},$$

where a' and a_0' are defined as the *activities* in the corresponding states. As the pressure of S vapour decreases and approximates to the ideal state, we shall complete the above definition by saying that a' approaches c. If we write $\frac{a'}{a_0'} = a$, an equation defining a, the *relative activity*, then

$$\bar{F} - F_0 = RT \log a. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* The term "free energy" is used here to mean the quantity $u - T\phi + pv$, where u = total energy, ϕ = entropy, p = pressure, v = volume.

At the standard state the value obtained from equation (2) must be zero; hence $\log a=0$ and $a=1$. For an increase of pressure equation (2) gives

$$\left(\frac{\partial \overline{F}}{\partial P}\right)_T = RT\left(\frac{\partial \log a}{\partial P}\right)_T \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Combining (1) and (3),

$$\left(\frac{\partial \log a}{\partial P}\right)_T = \frac{V_S}{RT}.$$

Integrating this equation from $P=p_S$, where p_S is the pressure of pure S vapour in equilibrium with the condensed phase at the temperature T, to $P=P$,

$$(\log a)_{P=P} - (\log a)_{P=p_S} = \frac{V_S}{RT}(P-p_S), \quad . \quad . \quad . \quad (4)$$

if the compressibility of the solid (or liquid) substance S is sufficiently small that it may be neglected. If the standard state of pure S vapour be chosen as that in equilibrium with solid (or liquid) S at T, then by definition $(\log a)_{P=p_S}=0$, and equation (4) becomes

$$\log a_P = \frac{V_S}{RT}(P-p_S).$$

When P becomes large compared to p_S, this equation may be written

$$\log a_P = \frac{PV_S}{RT}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where P is the partial pressure of the indifferent gas.

Since by supposition the concentration of S vapour in E is small, it may be supposed to conform to the ideal gas laws with sufficient approximation, and thus $a'=c$ for the pure vapour phase E. Owing to the presence of the indifferent gas in B, which may be at high pressure and concentration, it does not follow that in the gas+vapour phase $a'=c$. Introducing an activity coefficient defined by the equation $a'=f'c$, then

$$\frac{a'}{a_0'} = a = \frac{f'c}{f_0'c_0},$$

and by putting $\frac{f'}{f_0'}=f$, where f is the *relative activity coefficient*,

$$a_P = f_P \cdot \frac{c_P}{c_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and from equations (5) and (6)

$$\log f_P = \frac{PV_S}{RT} + \log c_0 - \log c_P. \quad . \quad . \quad . \quad . \quad (7)$$

Hence, if from the experimental data c_P as a function of P be known, f_P as a function of P can be determined, and the deviation from the ideal gas laws of S vapour in its admixture with the indifferent gas ascertained.

If C, in fig. 1, consists of two solid phases possessing a definite equilibrium vapour pressure for a given temperature, *e.g.* $Na_2SO_4 10H_2O$—Na_2SO_4, the calculations and formulæ are analogous to those given above. The reversible reaction occurs according to the equation

$$Na_2SO_4 10H_2O \rightleftarrows Na_2SO_4 + 10H_2O.$$

If, at the pressure P and the temperature T, F_1 be the molar free energy of $Na_2SO_4 10H_2O$. F_2 the molar free energy of Na_2SO_4, and $\bar{F}$ the partial molar free energy of H_2O vapour in its admixture with the indifferent gas, then for equilibrium

$$F_1 = F_2 + 10\bar{F}$$

and

$$\left(\frac{\partial \bar{F}}{\partial P}\right)_T = \frac{1}{10}\frac{\partial}{\partial P}(F_1 - F_2)_T = \frac{V_1 - V_2}{10}, \quad . \quad . \quad . \quad (8)$$

where V_1 is the molar volume of $Na_2SO_4 10H_2O$, and V_2 the molar volume of Na_2SO_4. From (3) and (8)

$$\left(\frac{\partial \log a}{\partial P}\right)_T = \frac{V_1 - V_2}{10RT}.$$

By a similar reasoning to that employed in the previous case,

$$\log a_P = \frac{V_1 - V_2}{10RT} \cdot P, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

the standard state being defined as that of pure water vapour in equilibrium with the solid phases at the temperature T. The compressibilities of the solid phases are small and may be neglected without appreciable error. As an approximation, a_P may be put equal to $\frac{c_P}{c_0}$; whence

$$\log \frac{c_P}{c_0} = \frac{V_1 - V_2}{10RT} \cdot P, \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

and, if c_0 be known, the concentrations at various pressures of the indifferent gas may be calculated with the validity involved in the assumption that $a_P = \frac{c_P}{c_0}$. From equations (6) and (9),

$$\log f_P = \frac{V_1 - V_2}{10RT} \cdot P + \log c_0 - \log c_P, \quad . \quad . \quad (10)$$

and $\log f_P$ may be determined as a function of P, if, from the experimental data, c_P is known as a function of P.

As the pressure of the indifferent gas increases, f will be subject to two influences:

(*a*) An intermolecular attraction or association between the molecules of S vapour and those of the indifferent gas.

(*b*) A diminution of the space available for the molecules of S vapour, owing to the increasing space occupied by the molecules of the indifferent gas.

In the case of a *pure* gaseous substance these two influences were considered by van der Waals, and are embodied in his well-known equation,

$$p = \frac{RT}{v-b} - \frac{a}{v^2}.$$

If p_i denote the pressure of a gas, supposed ideal, at the same volume v and temperature T,

$$p_i = \frac{RT}{v},$$

and therefore

$$\frac{p}{p_i} = \frac{v}{v-b} - \frac{a}{RTv}.$$

As p increases and v diminishes, $\frac{p}{p_i}$ will at first diminish owing to the effect of the second term, whilst when v becomes sufficiently small, $\frac{p}{p_i}$ will increase owing to the preponderating effect of the first term. The following table ('Thermodynamics,' Lewis and Randall, p. 196) shows this behaviour for Oxygen at 0° C.:—

P Atm.	p/p_i.	Fugacity-coefficient.
50	0·961	0·960
100	0·929	0·925
200	0·91	0·87
400	1·05	0·85
600	1·29	0·90

From the second column it is evident that the ratio p/p_i for oxygen begins to increase at some pressure between 200 and 400 atmospheres. The third column gives the value of $\frac{\text{fugacity}}{\text{pressure}}$, a quantity which is closely related to the activity

coefficient in the preceding. The fugacity coefficient decreases to a minimum value at some pressure between 400 and 600 atmospheres, and then increases. If the vapour of C in E does not obey the ideal gas laws, the activity coefficient would vary with the pressure in this manner. The argument can be applied only to pure gaseous systems, but it seems probable that in the mixture of S with the indifferent gas the first effect of increasing the concentration of the latter would be to decrease the activity of S. The result of this would be a greater increase in the concentration of S with increasing pressure of the indifferent gas than would be given by an equation such as (9 *a*). It is very probable, therefore, that the first effect of increasing the pressure of the indifferent gas would be to decrease the value of $\log f$ as experimentally determined.

The Method.

The system chosen for the investigation was

$Na_2SO_4 10H_2O$—Na_2SO_4—water vapour at 25° C.,

the indifferent gas used being air. The air was maintained in contact with the sodium sulphate, at constant pressure and temperature, until equilibrium was established between the partial pressure of the water vapour it contained and the dissociation pressure of the solid phases. A small amount of this air containing water vapour was released to atmospheric pressure and the amount of water vapour in a known volume determined.

The pressure was accurately determined by means of a gauge in which a Cailletet tube, mounted in a suitable mercury-filled steel block, was employed. The tube was filled with a known volume of pure hydrogen, and the pressure determined from the diminution of the volume of the hydrogen.

The water vapour was removed from the air in a specially designed condensation tube. It consisted of a U-tube connected to a mercury manometer, in one limb of which was a constant volume pointer. The volume of the condensation tube to the tip of this pointer was accurately determined. The water vapour was removed from the air by passing it through the U-tube, which was immersed in liquid air. While the tube was still maintained at the temperature of liquid air it was closed off from the remainder of the apparatus and evacuated to a pressure of 1×10^{-6} mm. of mercury. The condensation tube was

then closed off from the evacuating system and heated to such a temperature that the water frozen out was completely converted into vapour, and its pressure as such measured. The pressure, volume, and temperature of the water, as vapour, are known, and assuming that at such low pressures (20 mm.) water vapour behaves as an ideal gas with sufficient approximation, its mass may be calculated. The method was carefully tested, and it was found that the error involved was 1 part in 1000.

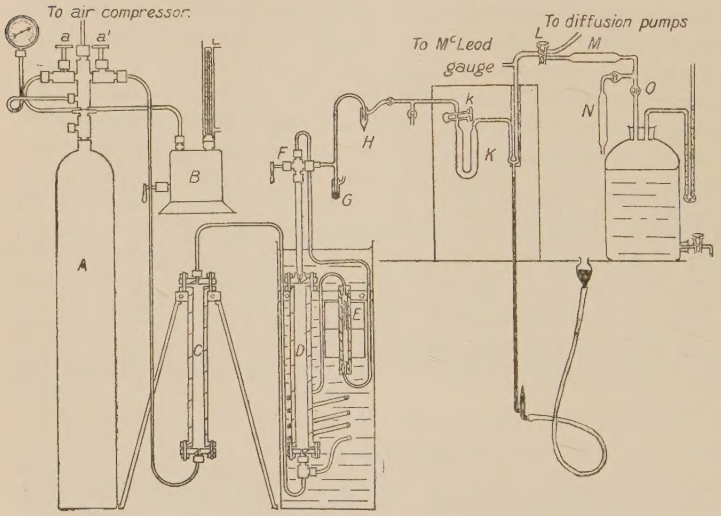
It was found that diffusion alone was not sufficient to establish equilibrium between the partial pressure of the water vapour in the air under pressure and the dissociation pressure of the solid phases with the necessary rapidity, and a device for circulating the air under pressure was employed. The device worked on the principle of the ordinary lift pump with the usual arrangement of valves. The piston was of soft iron, the cylinder of gunmetal and of suitable dimensions to withstand the pressures used. The oscillatory movement of the piston was produced by the agency of a series of solenoid coils wound on the outside of the gunmetal cylinder. The requisite coils were energised by means of a motor-driven commutator. The device was an integral part of the vessel containing the sodium sulphate, and operated in such a way as to provide continuous circulation of the same air upwards through the mixture of the solid phases, downwards through the circulator, to again pass through the sodium sulphate. By the employment of this device equilibrium was readily established within the saturator.

The Apparatus.

The apparatus used is shown diagrammatically in fig. 2. The air was supplied by a motor-driven air compressor. The air, after being compressed, passed through a KOH cylinder from which connexion was made to the apparatus by copper capillary tubing. A is a steel cylinder of about 45 litres capacity with valves, gauges, fittings, and pressure-line leading from the compressor as shown. The valve a is a release valve, a' closes the connexion between A and the remainder of the apparatus. The arrangement of a and a' together with the valve in the cylinder A permitted the releasing of pressure from any portion of the apparatus desired, the remaining parts being still maintained at full pressure. The Bourdon gauge was used for the preliminary adjustment of pressure. Accurate readings of pressure

were made on the gauge B connected to the open end of the valve *a*. The cylinder A and the gauges are connected by steel capillary tubing from *a'* to the bottom end of C, which is a steel cylinder containing phosphorus pentoxide. The top end of C is connected by similar steel tubing to the bottom end of a similar steel cylinder D, which was filled with a mixture of equal parts of $Na_2SO_4 10H_2O$ and Na_2SO_4 interspersed with sufficient glass-wool to prevent the substance packing tightly together. A second filling was used in which the glass-wool was omitted. The salt used was the purest commercially obtainable and, as measurements of its dissociation pressure at a pressure of one atmosphere agreed

Fig. 2.



with the accepted values, was sufficiently pure for the purpose of such a measurement. A pipe of $\frac{3}{4}$ inch external diameter with an $\frac{1}{8}$-inch bore was fitted into the top end of the cylinder D, to which was attached a reducing valve at F. The circulator is shown at E. The copper capillary from the bottom of the pump was joined at F; the capillary from the top end was about 12 feet long, was coiled into a spiral around D and then joined to a T-piece in the capillary connecting C to D, just below its union to the bottom end of the cylinder D. The long length of capillary tubing is necessary to overcome any heating effect due to the pump and to ensure that the temperature of the air entering D is that of the thermostat. The cylinder D together with

the circulating pump and connexions were immersed in an oil thermostat maintained at $25 \pm 0°{\cdot}05$ C. The projecting portion F was covered by a hood through the side of which the valve handle protruded. A carbon filament lamp inside the hood kept the connecting tubes above the temperature at which condensation could occur.

A glass to metal join at F connects the high-pressure portion of the apparatus to the condensation tube etc. G is a mercury safety valve which prevents excessive pressures developing within the glass tubing. H is a trap to prevent mercury being forced over into the condensation tube, should the connecting taps be inadvertently opened when K is evacuated. K is the condensation tube. It was mounted permanently in an air thermostat provided with plate-glass windows back and front so that readings of pressure could be made. The front was so arranged that it could be removed. The temperature was maintained and controlled electrically. The thermoregulator could be adjusted to temperatures from 10° to 40° C. Connexions to the diffusion pumps and the McLeod gauge were as shown in the diagram. The tube M was filled with phosphorus pentoxide. A side tube between M and the tap O provided with a tap permitted connexion being made to the tube N, which was open to the atmosphere. The lower half of N was filled with soda-lime, the remainder with phosphorus pentoxide. An aspirator bottle provided with a water manometer and with a thermometer suspended inside completed the apparatus.

Experimental Procedure.

The apparatus to F was raised to the required pressure by means of the air compressor and the pressure-line was cut off at the compressor. The cylinder A is left connected through to D, the needle valve in the gauge B remaining closed except during a reading of the pressure. The oil thermostat and the circulator were maintained in continuous operation. After the thermostat has been at constant temperature, and the air at constant pressure, overnight, the valve F is opened slightly and air from D is allowed to pass slowly through the apparatus, escaping through N. Sufficient air is allowed to escape so that the apparatus from F to *k* is filled with air released from D, and also that the surface of the glass is in equilibrium with this air. *k* and F are closed and K is filled with dry air by evacuating the apparatus from *k* to L and releasing the vacuum slowly through N. K is now immersed in liquid air. When sufficient time has elapsed for the air

in K to have reached the temperature of liquid air and the accompanying decrease of pressure to be adjusted, F is opened slightly and the rate of flow regulated by the rate at which the released air bubbles through the mercury in G. The tap N is closed, O is opened, and finally *k* is opened. Water is then run from the aspirator bottle at from 2 to 3 litres per hour. It was found by experiment that at rates up to 5 litres per hour consistent results could be obtained at any one pressure. The rate of flow of air through K is controlled entirely by the rate at which the water is removed from the aspirator, as it is immaterial during a run whether or not some of the air released at F escapes through G. As a safeguard against any possible leakage between F and *k*, a pressure of from 10 to 15 cm. of water was maintained within the apparatus, so that if there were a leak gas would escape. The escape of air from this portion of the apparatus would make no difference in the final result, but a very small amount of air drawn into the apparatus would give altogether too high a value.

The position of the mercury meniscus in the gauge B is read off on the scale by means of the cathetometer, as is also the position of the top end of the tube, and the pressure determined by reference to the calibration curve for the gauge. The pressure indicated by the Bourdon gauge is also noted.

Sufficient water is run out of the aspirator, so that the amount of water frozen out in K will, when heated to a temperature of 40° C., give a pressure between 20 and 25 mm. of mercury. When sufficient water has been removed from the aspirator *k* is closed and then F is closed. The pressure from the aspirator to *k* is then reduced to that of the atmosphere by running water from the aspirator. The total number of c.c. of water removed from the aspirator is noted and the temperature of the aspirator read. The pressure is again determined from the gauge B, and the mean of the two readings of the accurate gauge, in which the greatest deviation is never more than 0·2 atmosphere, is taken as the hydrostatic pressure on the sodium sulphate, after correction has been applied for the difference in level between the mercury meniscus in the capillary tube of the pressure gauge and that in the reservoir of the gauge. K is then evacuated very slowly by means of the water-pump and evacuation continued by the diffusion-pumps to as low a value as possible. It is necessary to carry out the first part of the evacuation very slowly, as otherwise some of the minute crystals of ice frozen out in K might be carried

away, and, since the total amount present is very small, such a loss would introduce a considerable percentage error into the final result. The barometric pressure is then read. The mercury is raised into the manometer tube of K, the liquid air removed, and K permitted to come to room temperature. The U is then dried with a cloth and the thermostat closed and set in operation. The pressure in K was measured at successively lower temperatures until the pressures differed by a constant value or were equal to the vapour pressure of water at these temperatures. When such is the case, the pressure measured is the vapour pressure of water condensed on the walls of the tube and is not affected by the adsorption of water from the gas phase. If the pressure is higher than the vapour pressure of water there must be some other gas present, and at the higher temperatures the pressures measured must be corrected for this amount. The temperature is then increased until the pressures read at successively increasing temperatures are increasing proportionally with the absolute temperature. The results are expressed as the number of millimoles of water per litre of dry air measured at the pressure P (the pressure of air in contact with the sodium sulphate). These may be considered as the number of millimoles of water per litre of space in D without appreciable error.

If P is the pressure in atmospheres; V the number of c.c. of water removed from the aspirator at a temperature T_v; p the pressure in K due to water vapour corrected to that of mercury at 0° C. and measured at the temperature T_a; (PV) the product of pressure and volume calculated from the data of Amagat (*Ann. de Chim. et Physique*, xix. p. 375, 1880), the value of this product for 1 c.c. of air at a pressure of 1 atmosphere and a temperature of 25° C. being taken as unity; B the barometric pressure corrected to mercury at 0° C. and for the vapour pressure of water at T_v° C., the moles per litre are calculated as follows. Putting the volume of the condensation tube equal to A, the amount of water expressed as moles equals

$$\frac{273 \cdot A \cdot p}{22410 \cdot 760 \cdot T_a}$$

The volume of air collected, calculated to a pressure of P atmospheres and a temperature of 25° C., equals

$$\frac{298 \cdot V \cdot B \cdot (PV)}{760 \cdot T_v \cdot P} \text{ c.c.}$$

The millimoles per litre of dry air measured at P atmospheres is

$$\frac{1000 \cdot 273 \cdot 1000}{298 \cdot 22410} \cdot \frac{A \cdot T_v P p}{VB(PV)T_u}.$$

The Accuracy of the Apparatus.

The various terms in the equation above were determined with the following accuracy :—P to 0·1 atmosphere ; T_v to 0°·1 C. ; p to 0·01 mm. ; V to 5 c.c. ; B to 0·1 mm. ; T_u to 0°·05 C. ; A to 0·01 c.c. ; the temperature of the oil thermostat to 0°·05 C. The values of (PV) are taken as being accurate to 1 in 4000. By differentiating the equation given above and substituting these variations for the corresponding differentials, the probable error of the apparatus is 0·2 per cent.

The Results.

The readings obtained in the various measurements are given in Table I. The significance of the various symbols has been given previously with the exception of B.p., which is the barometric pressure as read at the temperature given. Table II. column 2 gives the concentration of water in millimoles per litre of air measured at the pressure P, calculated from the data in Table I. The values calculated from equation (9 *a*) at the corresponding pressures are given in Table II. column 3. The results are shown graphically in fig. 3, in which the values of P are plotted as abscissæ and the number of millimoles per litre as ordinates. The value of the concentration of water in the gas phase when the pressure on the system is that defined as the standard state is given by the horizontal line marked "standard." The calculated values are also given. The plotted values give two distinct curves. From 24·4 to 77·6 atmospheres there are apparently two possible values of the concentration at any one pressure. In this region values have been obtained which fall between these two curves. At all other pressures the values agree within 0·2 per cent., which was the probable error calculated for the apparatus.

The concentrations given in Table II. were obtained from measurements of two fillings of sodium sulphate, the first of which was interspersed with glass-wool, the second in which only the crystals of the hydrated and the anhydrous salt were present. The measurements on the first sample were begun at the higher pressures, above 77·6 atmospheres. The temperature and pressure were maintained constant for

TABLE I.

P Atm.	T_u °C.	*p* mm.	T_v °C.	V c.c.	B.p. at °C.		(PV.)
2·7	39·0	22·34	13·7	70	757·2	17·5	0·9992
5·1	39·2	20·95	12·5	118	763·6	17·0	·9987
9·3	39·2	22·80	17·0	232	763·8	19·5	·9972
15·1	39·2	24·40	14·9	389	774·3	18·0	·9942
15·4	39·2	26·02	15·8	424	772·5	18·5	·9942
16·5	39·0	24·24	17·5	441	752·8	17·0	·9939
17·3	40·0	16·77	23·0	324	765·5	22·0	·9936
22·3	39·2	21·42	14·9	524	770·5	16·0	·9916
23·8	39·2	19·35	15·3	536	764·3	17·0	·9910
23·9	39·2	18·89	16·3	523	752·2	17·0	·9909
24·4	39·1	19·48	14·3	525	769·8	17·0	·9908
24·6	38·8	18·65	18·2	523	762·1	18·0	·9908
24·7	39·0	16·78	14·2	457	772·0	16·5	·9908
25·0	39·1	30·31	17·1	701	762·7	19·0	·9905
25·2	35·0	17·48	20·1	532	757·4	19·0	·9905
25·2	35·5	17·30	18·1	524	755·4	17·0	·9905
25·3	33·0	17·35	17·2	532	749·0	18·0	·9904
25·4	39·1	28·60	16·1	671	771·0	18·5	·9904
25·6	35·0	16·62	20·0	522	755·4	19·0	·9903
25·7	39·0	18·26	17·2	532	760·4	17·0	·9901
25·8	36·2	20·25	15·0	518	767·7	17·0	·9901
25·8	35·0	17·60	18·4	548	746·5	18·0	·9901
25·8	39·2	19·33	18·2	537	758·4	18·0	·9901
25·9	39·1	24·63	15·5	662	773·4	18·5	·9901
26·0	35·2	16·60	18·8	543	761·2	18·0	·9900
26·2	35·0	16·24	18·2	533	755·4	18·0	·9900
26·3	36·9	21·64	15·2	644	766·7	18·0	·9900
26·9	36·0	18·28	16·5	624	754·5	17·5	·9897
27·7	35·4	19·23	18·5	631	756·9	18·0	·9887
28·1	36·1	16·60	18·2	633	752·6	17·5	·9886
29·4	36·2	19·71	18·1	735	749·3	18·0	·9874
29·9	36·0	23·40	18·6	853	755·3	18·0	·9872
30·4	36·7	21·84	18·7	836	760·6	18·0	·9872
30·6	39·0	23·70	15·5	857	773·0	18·5	·9870
33·1	38·0	16·77	17·8	773	766·3	17·0	·9868
33·2	39·3	24·97	14·9	1064	759·0	18·0	·9868
36·1	37·6	16·71	22·5	825	769·1	21·5	·9864
40·9	39·0	17·87	22·0	1028	772·3	21·0	·9847
41·5	36·6	24·41	19·1	1537	769·7	21·0	·9846
42·8	39·3	27·25	14·3	1566	757·8	18·5	·9842
44·0	38·0	17·15	20·5	1030	769·7	20·5	·9838
45·6	39·3	25·88	15·6	1554	771·8	18·0	·9837
46·4	38·6	15·71	19·7	1028	767·9	19·7	·9834
48·0	36·0	16·08	17·3	1053	749·0	18·5	·9830
49·2	36·5	18·37	20·3	1240	761·2	19·5	·9828

TABLE I. (*continued*).

P Atm.	T_u °C.	p mm.	T_v °C.	V c.c.	B.p. at °C.		(PV.)
55·2	39·2	25·80	18·1	2073	765·0	17·0	0·9811
57·1	39·2	28·84	18·1	2562	750·9	16·0	·9811
62·4	39·1	25·60	18·2	2400	760·2	17·0	·9811
64·6	39·6	23·72	19·5	2021	743·6	20·0	·9811
66·7	38·7	23·10	18·3	2305	752·2	16·5	·9811
67·2	39·2	23·16	18·8	2057	769·2	17·5	·9811
67·4	39·9	23·29	16·7	2016	767·4	18·0	·9811
70·0	39·3	25·78	19·0	2663	752·4	18·0	·9810
71·5	38·6	25·40	18·8	2562	772·8	20·0	·9810
72·2	39·5	24·65	18·0	2560	753·0	16·0	·9810
72·5	39·6	25·26	17·4	2570	753·1	16·5	·9810
75·0	39·5	26·56	19·8	2840	757·3	19·0	·9809
75·8	39·2	25·15	17·6	2692	753·4	16·0	·9809
76·3	39·8	26·33	18·9	2760	772·5	21·0	·9808
77·6	39·7	28·13	19·6	3030	754·5	18·0	·9808
81·3	39·6	20·34	20·0	2046	763·4	18·0	·9806
83·8	40·3	23·30	17·7	2610	765·6	16·0	·9806
88·6	39·6	22·81	17·2	2685	761·0	16·0	·9806
92·6	39·2	23·60	17·1	2880	760·0	16·0	·9809
98·4	39·9	24·13	17·2	3070	763·5	16·0	·9818

The volume of the condensation tube was 26·58 c.c. at the following pressures:—2·7; 5·1; 9·3; 15·1; 15·4; 16·5; 22·3; 23·8; 23·9; 24·4; 24·7; 25·0; 25·3; 25·4; 25·7; 25·8; 25·9; 26·3; 26·9; 30·6; 33·2; 42·8; 45·6; 48·0; 64·6; 67·4.

26·75 c.c. at 17·3; 24·6; 25·2; 25·6; 25·8; 26·0; 27·7; 33·1; 36·1; 41·0; 46·4; 49·2; 67·2; 81·3.

And 29·58 c.c. at 41·5; 55·2; 57·1; 62·4; 66·7; 70·0; 71·5; 72·2; 72·5; 75·0; 75·8; 76·3; 77·6; 83·8; 88·6; 92·6; 98·4.

20 hours before a measurement was made. Determinations were made both with increasing and decreasing pressures of air. Proceeding in this manner, the portion of the curve from 100 to 77·6 atmospheres was obtained. At 77·6 atmospheres there was a sharp break in the curve, and to 40 atmospheres the lower curve was obtained. A peculiar effect was observed between 40 and 55 atmospheres. If the pressure were increased from 1 atmosphere to any pressure between 40 and 55 atmospheres, and the temperature and pressure were maintained constant for 20 hours, a subsequent determination of the concentration gave values which fell along the upper linear curve; but if the temperature and pressure were maintained constant for a further

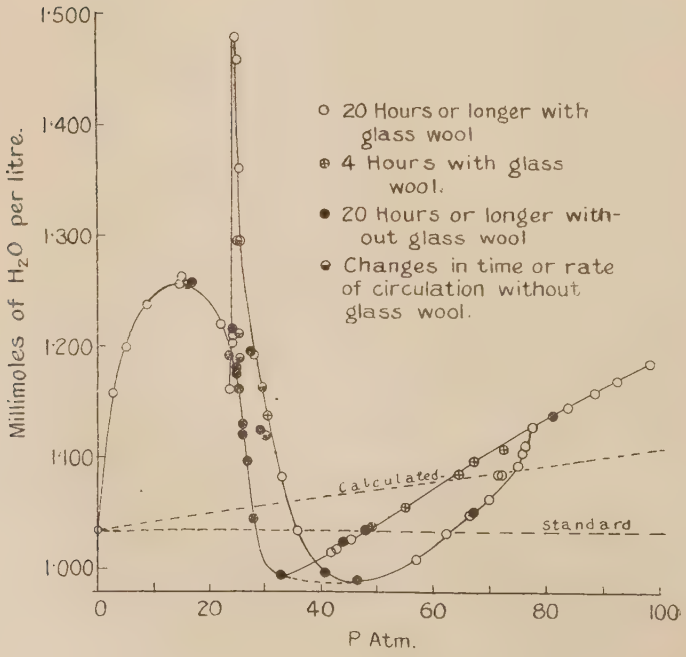
TABLE II.

P Atm.	Millimoles of H_2O per litre. Found.	Calculated.	log *t*.
2·7	1·158	1·036	−0·0486
5·1	1·200	1·038	− ·0632
9·3	1·238	1·040	− ·0756
15·1	1·255	1·045	− ·0795
15·4	1·262	1·045	− ·0831
16·5	1·255	1·046	− ·0793
17·3	1·257	1·047	- ·0796
22·3	1·219	1·050	− ·0647
23·8	1·161	1·051	- ·0433
23·9	1·191	1·051	− ·0544
24·4	1·202	1·052	− ·0579
24·6	1·215	1·052	− ·0628
24·7	1·208	1·052	− ·0602
25·0	1·477	1·052	− ·1475
25·2	1·180	1·052	− ·0496
25·2	1·175	1·052	− ·0479
25·3	1·172	1·052	− ·0470
25·4	1·458	1·052	− ·1416
25·6	1·161	1·053	− ·0445
25·7	1·211	1·053	− ·0611
25·8	1·359	1·053	− ·1109
25·8	1·189	1·053	− ·0149
25·8	1·293	1·053	− ·0891
25·9	1·294	1·053	− ·0897
26·0	1·120	1·053	− ·0267
26·2	1·130	1·053	− ·0309
26·3	1·192	1·053	− ·0540
26·9	1·097	1·053	− ·0180
27·7	1·195	1·054	− ·0544
28·1	1·045	1·054	+ ·0039
29·4	1·124	1·055	− ·0273
29·9	1·163	1·055	− ·0422
30·4	1·117	1·056	− ·0242
30·6	1·137	1·056	− ·0321
33·1	0·993	1·058	+ ·0275
33·2	1·081	1·058	− ·0092
36·1	1·034	1·060	+ ·0110
40·9	0·996	1·063	+ ·0287
41·5	1·017	1·063	+ ·0196
42·8	1·018	1·065	+ ·0197
44·0	1·026	1·066	+ ·0166
45·6	1·026	1·067	+ ·0173
46·4	0·990	1·068	+ ·0327
48·0	1·038	1·069	+ ·0121
49·2	1·037	1·070	+ ·0134

TABLE II. (*continued*).

P Atm.	Millimoles of H_2O per litre. Found	Calculated.	log *f*.
55·2	1·059	1·074	+0·0061
57·1	1·008	1·075	+ ·0285
62·4	1·032	1·079	+ ·0197
64·6	1·085	1·081	− ·0015
66·7	1·049	1·083	+ ·0137
67·2	1·051	1·083	+ ·0131
67·4	1·097	1·083	− ·0056
70·0	1·063	1·085	+ ·0089
71·5	1·085	1·086	+ ·0003
72·2	1·085	1·086	+ ·0007
72·5	1·108	1·087	− ·0086
75·0	1·093	1·089	− ·0017
75·8	1·104	1·089	− ·0058
76·3	1·111	1·090	− ·0083
77·6	1·127	1·091	− ·0138
81·3	1·136	1·094	− ·0165
83·8	1·144	1·095	− ·0190
88·6	1·158	1·099	− ·0225
92·6	1·169	1·102	− ·0257
98·4	1·184	1·107	− ·0293

Fig. 3.



period of 20 hours, values along the lower curve were obtained. When the pressure and temperature were maintained constant for still longer periods, the values obtained were those on the lower curve. At pressures from 40 to 25 atmospheres the concentrations increased very rapidly with decreasing pressure, reaching a very high maximum at 25 atmospheres. The values from 30 to 25 atmospheres were obtained over a period of 5 days, during which time the thermostat was in operation night and day, maintaining constant temperature throughout this period. Readings were made each day, and the only decrease of pressure during this time was due to the removal of air in making the necessary measurements, and to any leakage in the high-pressure portion of the apparatus. The decrease of pressure was of the order of 0·3 atmosphere in 24 hours. It was thought that some portion of the apparatus might be at fault during this series of measurements, and between each successive measurement of concentration some portion of the apparatus was altered the U-tube K was removed and thoroughly cleaned, the phosphorus pentoxide in the glass portion of the apparatus and in the steel cylinder C was replaced, and fresh soda-lime placed in the tube N; but these various changes had no effect on the concentrations measured. The same conditions of temperature and pressure were maintained from 25 to 23·8 atmospheres, and down to this pressure the concentration of water in the gas phase decreased very rapidly with decreasing pressure. The pressure was then increased to 45 atmospheres, and a measurement at this pressure gave a value agreeing with those already obtained. With decreasing pressure the curve to 25 atmospheres was again obtained. From 23·8 atmospheres downwards the concentrations increased with decreasing pressure, passing through a maximum at 16 atmospheres and then decreasing rapidly to 2·7 atmospheres. Readings below 2·7 atmospheres were not obtained owing to the difficulty of measuring the pressure with sufficient accuracy with the apparatus available. The interpolation of the curve from 2·7 atmospheres to standard pressure is, however, justified from the shape of the curve. Two series of measurements were made from 23·8 to 2·7 atmospheres and agreeing results were obtained. The concentrations gave 4 portions of curves: that from the standard pressure to 23·8 atmospheres with a maximum at 16 atmospheres, that from 23·8 to 77·6 atmospheres with a very high maximum at 25 atmospheres and a minimum at 45 atmospheres (the concentration at this pressure being below the standard

value), the almost linear portion from 77·6 to 100 atmospheres, and a short portion between 40 and 55 atmospheres which appeared to be a continuation of that portion above 77·6 atmospheres. Since, between 40 and 55 atmospheres, the time during which temperature and pressure were maintained constant was the deciding factor on the value of the concentration obtained, it was thought that, by altering the length of time of these conditions between 55 and 77·6 atmospheres, different values of the concentration of water in the gas phase might be obtained. Measurements were made at 55·2, 64·6, 67·4, and 72·5 atmospheres, temperature and pressure being maintained constant for 4 hours before making the determination. The values obtained when plotted gave the upper almost linear curve from 40 to 100 atmospheres. Similar variations were made in the times during which temperature and pressure were maintained constant at pressures between 40 and 2·7 atmospheres, but the results agreed with those obtained after temperature and pressure had been maintained constant for 20 hours or longer. If the concentrations representing a stable state in the system be taken as those which are obtained with temperature and pressure constant over periods of several days, then in the figure the curves representing this stable state will be, that from 2·7 to 23·8 atmospheres, the upper almost vertical portion from 23·8 to 25 atmospheres, the continuous curve from the high maximum at 25 atmospheres passing through a minimum at 45 and again increasing to 77·6 atmospheres, and the portion from 77·6 to 100 atmospheres. The portion from 40 to 77·6 atmospheres, the upper linear curve, would then represent some metastable condition.

The procedure adopted with the second filling, in which the glass-wool was omitted, was to maintain temperature and pressure constant for 20 hours, as before, but to begin at the lower pressures and to trace the curve with increasing pressure. The results were identical with those of the first filling up to 24·4 atmospheres, the concentration increasing rapidly with increasing pressure, passing through the same maximum at 16 atmospheres and then decreasing to 24·4 atmospheres. From 24·4 to 40 atmospheres the values did not, however, agree with those of the first filling; the values now found, instead of increasing with increasing pressure, decreased rapidly passing through a minimum at 33 atmospheres. This portion of the curve was then traced with decreasing pressure, the temperature of the thermostat being maintained constant over a period of 6 days, readings

being made each day ; the decrease of pressure being as before due to the air removed in making a measurement, and to any leakage in the high-pressure portion of the apparatus. The results obtained were still those along the lower curve from 24·4 to 33 atmospheres. Between pressures of 40 and 55 atmospheres the values were identical with those of the first filling : namely, with temperature and pressure constant for 20 hours the values along the upper curve were obtained, and with a further period of 20 hours the values along the lower curve were obtained. From 55 to 77·6 atmospheres the results again agreed with those of the first filling ; with temperature and pressure constant for 20 hours the values along the lower curve were obtained, whilst with temperature and pressure constant for 4 hours the values along the upper curve were obtained. From 77·6 to 100 atmospheres the results were identical with those of the first filling.

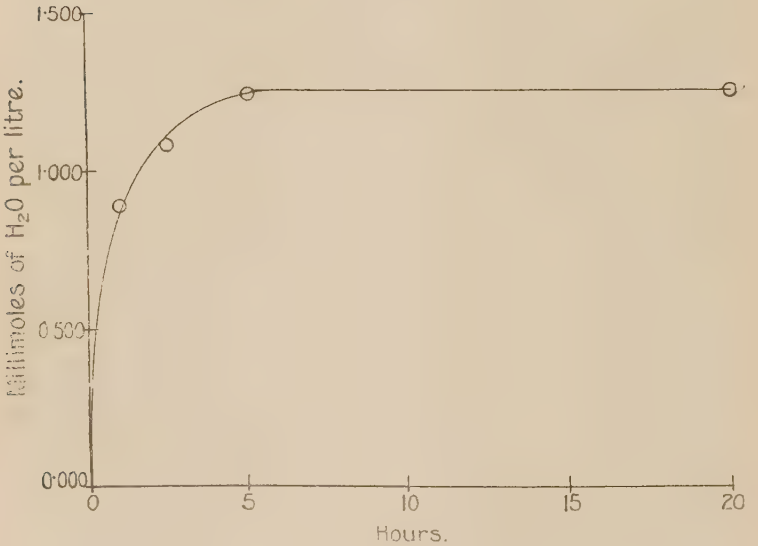
The temperature and pressure were maintained constant at 70 atmospheres for 20 hours ; the pressure was then increased to 81·3 atmospheres, maintained constant for 4 hours, and a measurement of the concentration made. The value obtained agreed with all previous measurements. Measurements made with temperature and pressure constant for shorter periods of time gave very low values indicating that equilibrium had not been reached. There was no indication that the conditions represented by the lower curve from 40 to 77·6 atmospheres persisted above the latter pressure. A series of measurements was then carried out at pressures very near to 25·8 atmospheres, in which the time during which temperature and pressure were maintained constant before making the determination as well as the rate of circulation were varied. A similar series was also carried out at 30 atmospheres pressure. The results are shown in Table III.

TABLE III.

P Atm.	Rate of circulation.	Time.	Millemoles per litre.
		No. 1.	
25·6	Fast	20 hours	1·161
25·8	Slow	20 „	1·189
25·7	Slow	4 „	1·211
25·8	Slow	1½ „	1·293
		No. 2.	
28·1	Fast	20 hours	1·045
30·4	Slow	20 „	1·117
29·9	Slow	4 „	1·163

In the two series in Table III. the rate of circulation as well as the time during which temperature and pressure are maintained constant affect the values of the concentration obtained. In the first series the value at 25·8 atmospheres and $1\frac{1}{2}$ hours is several percent lower than the value on the upper curve at this pressure; but at 29·9 atmospheres and 4 hours (in No. 2) the value of the concentration is in agreement with those on the upper curve. Another series was carried out at 17·5 atmospheres. The circulation was maintained at the rate which produced the variations in the values of the concentration in the preceding series.

Fig. 4.



Measurements of concentration were carried out with temperature and pressure constant for $1\frac{1}{2}$, 3, 5, and 20 hour periods. The pressure (and temperature) had been constant overnight at a pressure of 40 atmospheres, and was reduced to 17·5 atmospheres $1\frac{1}{2}$ hours before the first determination was made. By this means the concentration of water present in the gas phase is reduced below the standard value. The results are shown graphically in fig. 4, which is an ordinary equilibrium type of curve showing that only the one equilibrium is possible at this pressure. The

accepted value at a pressure of one atmosphere was obtained with both fillings before any readings at other pressures had been made and after each series was completed.

If, as before, the equilibrium conditions be taken as those represented by the concentrations found after pressure and temperature had been maintained constant for 20 hours or longer, then, in fig. 3, the curves representing this stable state will be, that from the standard pressure to 24·4 atmospheres, the lower curve from 24·4 to 33 atmospheres, the lower curve from 50 to 77·6 atmospheres, and that from 77·6 to 100 atmospheres. At 40 atmospheres there may be a curious discontinuity in the curve representing the stable conditions, but it is possible that the curve from 33 to 50 atmospheres may be that represented by the dotted line. The upper linear portion from 40 to 77·6 atmospheres must, as before, be due to some metastable state in the system. A comparison of the results obtained with the two fillings shows a very peculiar effect due to the glass-wool. The curves representing stable equilibrium conditions in the system are identical in both cases from 2·7 to 24·4 atmospheres and from 40 to 100 atmospheres, but from 24·4 to 40 atmospheres, with glass-wool present, the curve representing the stable equilibrium is the upper one with a very high and sharp maximum at 25 atmospheres, while without glass-wool the curve representing the stable conditions in the system is the lower one with a minimum between 30 and 50 atmospheres.

It is beyond the scope of this paper to attempt to explain the anomalies observed, but a comparison with other results is of interest. Pollitzer and Strebel (*Zeitschr. physik. Chemie,* ex. p. 768, 1924) have determined the concentration of water in the gas phase in equilibrium with liquid water at 50° C. and in the presence of air at pressures up to 200 kg. per cm.^{2}. Their results show that the concentration increases with the pressure, the curve obtained when the concentrations per unit volume are plotted as a function of the pressure being very nearly a straight line, and in every case greater than that calculated. The values of $\log f$ calculated from their data by equation (7) are shown in fig. 5.

Assuming the system in the present research to be

$$Na_2SO_4\,10H_2O—Na_2SO\ —\text{water vapour}$$

at all pressures, the relative activity coefficient may be calculated. These values of $\log f$, calculated from the experimental data by equation (10), are given in column 4,

Fig. 5.

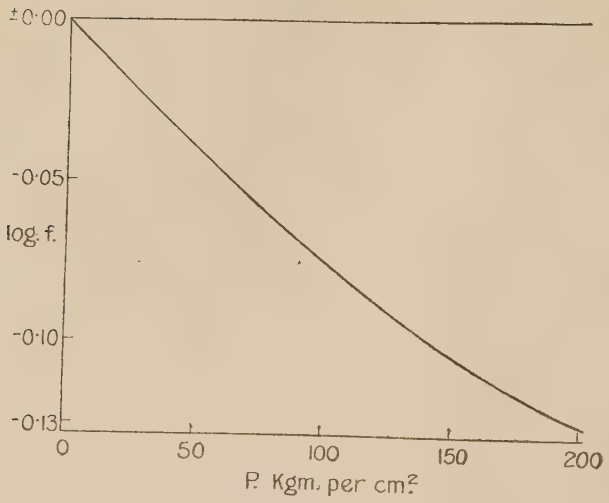

±0·00
-0·05
log. f.
-0·10
-0·13
0
50
100
150
200
P. Kgm. per cm²

Fig. 6.

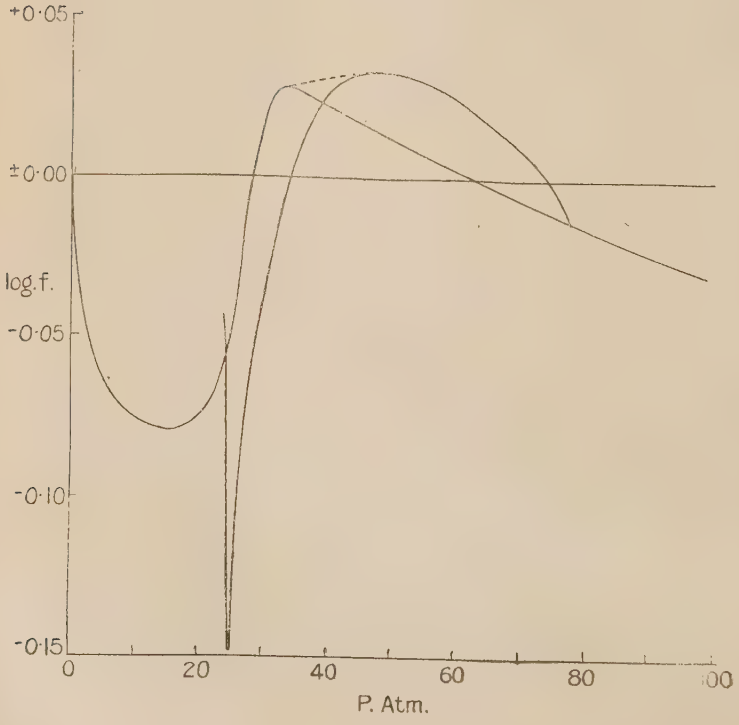

+0·05
±0·00
log. f.
-0·05
-0·10
-0·15
0
20
40
60
80
P. Atm.

Table II., and are shown graphically in fig. 6. In these deductions the effect of pressure of the indifferent gas on the value of the activity coefficient is taken as being entirely due to the deviation of water vapour from ideal gas behaviour as a result of the increasing density of the indifferent gas. If, however, the two solid crystalline phases (or either of them) should change, then their molar energies and free energies will change suddenly, and the plots of $\log a$, $\log c$, and $\log f$ will show breaks. Further discussion of the phenomenon must be postponed until other hydrate systems have been investigated.

The author wishes to express his thanks to His Majesty's Royal Commissioners for the Exhibition of 1851 for a scholarship during the carrying out of this research, to the Royal Society for a grant to aid in the purchase of apparatus, and to Professor F. G. Donnan, C.B.E., F.R.S., at whose suggestion the research was carried out, for his interest and instructive advice during the progress of the research.

Summary.

(1) The effect of the presence of an "indifferent" gas on the concentration and activity of a vapour in equilibrium with a condensed phase or system of condensed phases has been discussed thermodynamically.

(2) The relative activity coefficient for the vapour has been defined.

(3) The concentration of water in the gas phase in equilibrium with $Na_2SO^4 10H_2O$ and Na_2SO_4 has been measured in the presence of air up to a pressure of 100 atmospheres.

(4) The relative activity coefficient for water vapour in equilibrium with liquid water at 50° C. and in the presence of air up to a pressure of 200 kg. per cm.^{2} has been calculated from the date of Pollitzer and Strebel.

(5) The relative activity coefficient for water vapour in equilibrium with $Na_2SO_4 10H_2O$—Na_2SO_4 at 25° C. has been calculated, assuming that the effect observed is entirely due to the deviation of water vapour from ideal gas behaviour as a result of the increasing density of the indifferent gas.

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XLIX. *The Pressure of Radiation.* *By* W. F. G. Swann, *D.Sc., A.R.C.S., Professor of Physics in Yale University**.

THE calculation of the pressure on an absorbing or reflecting surface as the result of the incidence of radiation is one of the standard demonstrations of electromagnetic theory. There are two types of proof, one corresponding to that adopted in Planck's 'Wärmestrahlung' †, for example, for radiation reflected from a perfect conductor, and involving an actual calculation of the forces on the currents generated in the conductor by the combined action of the incident and reflected waves, and another proof of a more general type ‡, founded upon that equation of electrodynamics which is usually regarded as representing the law of the conservation of momentum. It is the latter proof which is the object of discussion in the present note, and which, in its usual statement, takes a form as follows :—

The Classical Derivation.

If **E** and **H** represent electric and magnetic vectors satisfying the electromagnetic equations, then,

$$\iiint\left(\mathbf{E}+\frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = -\frac{\partial}{\partial t}\iiint\frac{[\mathbf{EH}]_x}{c}d\tau + \iint(lp_{xx}+mp_{yx}+np_{zx})\,d\mathrm{S}\ ; \quad (1)$$

where

$$p_{xx}=\tfrac{1}{2}(\mathrm{E}_x^2-\mathrm{E}_y^2-\mathrm{E}_z^2+\mathrm{H}_x^2-\mathrm{H}_y^2-\mathrm{H}_z^2),$$
$$p_{yx}=p_{xy}=\mathrm{E}_y\mathrm{E}_x+\mathrm{H}_y\mathrm{H}_x,$$
$$p_{zx}=p_{xz}=\mathrm{E}_z\mathrm{E}_x+\mathrm{H}_z\mathrm{H}_x,$$

where, for simplicity of notation, we have, without loss of generality, confined ourselves to the x component of the momentum vector, and where the volume integrals are taken throughout a volume over whose surface the surface integrals are taken, l, m, n being the directional cosines of the outward normal.

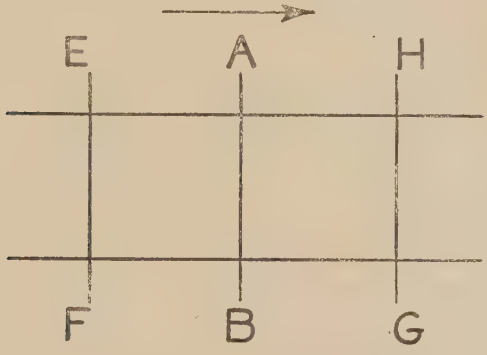
* Read at the Washington meeting of the American Physical Society, April 25–26, 1924. Communicated by the Author.

† *Wärmestrahlung*, 4th edition, pp. 50–56.

‡ Exemplified, for example, in H. A. Lorentz's 'Theory of Electrons,' pp. 28–29.

Suppose the arrow in fig. 1 represents the direction of the axis of x and of propagation of a plane wave. Let AB represent the material upon which the wave falls, and let the surface of integration be represented by unit areas EF and HG, and a cylindrical wall bounded in section by the lines EH and FG.

Fig. 1.



Since the wave is plane at EF and HG, the components E_x and H_x are zero there. Thus (1) reduces to

$$\iiint\left(\mathbf{E}+\frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = -\frac{\partial}{\partial t}\iiint\frac{[\mathbf{EH}]_x}{c}d\tau - \iint\frac{(\mathbf{E}^2+\mathbf{H}^2)}{2}d\mathrm{S}, \quad . \quad (2)$$

where $\mathbf{E}$ and $\mathbf{H}$ in the surface integrals represent resultant values, and where, in the other integrals it has not been necessary to invoke the question of whether or not E_x and H_x are zero everywhere.

Taking the time integral of the vector over a long time T, we have

$$\int_0^{\mathrm{T}} dt\iiint\left(\mathbf{E}+\frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = -\left[\iiint\frac{[\mathbf{EH}]_x}{c}d\tau\right]_0^{\mathrm{T}} - \int_0^{\mathrm{T}} dt\iint\frac{(\mathbf{E}^2+\mathbf{H}^2)}{2}d\mathrm{S}. \quad . \quad (3)$$

The average values may be obtained by dividing throughout by T.

From here the usual argument is to the effect that if the time T is sufficiently long, the first term on the right-hand side is sensibly zero compared with the

others since the motions are periodic, with the result that $\left[\iiint \frac{[\mathbf{EH}]_x}{c} d\tau\right]_0^T$ does not grow without limit with T. It thus results that

$$\frac{1}{T}\int_0^T dt \iiint \left(\mathbf{E} + \frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = -\frac{1}{T}\int_0^T dt \iint \frac{(\mathbf{E}^2+\mathbf{H}^2)}{2} d\mathrm{S}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The cylindrical wall of the boundary contributes nothing to the surface integral so that the right-hand side of (4) becomes

$$-\frac{1}{T}\int_0^T dt \left\{\left(\frac{\mathbf{E}^2+\mathbf{H}^2}{2}\right) \text{at HG} - \left(\frac{\mathbf{E}^2+\mathbf{H}^2}{2}\right) \text{at EF}\right\},$$

since HG and EF are supposed to represent surfaces of unit area.

Thus, if AB is a perfect absorber, so that **E** and **H** are zero at HG and equal to the values $\mathbf{E}_0$ and $\mathbf{H}_0$ for the primary wave at EF, we have

$$\frac{1}{T}\int_0^T dt \iiint \left(\mathbf{E} + \frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = \frac{1}{T}\int_0^T \frac{(\mathbf{E}_0^2+\mathbf{H}_0^2)}{2} dt, \quad . \quad (5)$$

while if the body AB is perfectly reflecting, **E** and **H** are zero at HG as before, but on account of the occurrence of the incident and reflected waves at EF, $\frac{1}{2}\iint(\mathbf{E}^2+\mathbf{H}^2)d\mathrm{S}$ has, for this case, twice the value for complete absorption, *i. e.*, twice the value $\frac{1}{2}\iint(\mathbf{E}_0^2+\mathbf{H}_0^2)d\mathrm{S}$, so that, for this case,

$$\frac{1}{T}\int_0^T dt \iiint \left(\mathbf{E} + \frac{[\mathbf{vH}]}{c}\right)_x \rho d\tau = \frac{1}{T}\int_0^T (\mathbf{E}_0^2+\mathbf{H}_0^2) dt, \quad . \quad (6)$$

Thus, the statement is made that, for the case of complete absorption, the pressure is equal to the energy per c.c. in the original wave, while for complete reflexion it is twice this amount.

Criticism of the Classical Derivation.

The vectors **E** and **H** in the surface integrals of the foregoing derivation refer to the total field, and it is as such that **E** and **H** figure in the volume integral of (6), which, of course, only receives contributions from the region occupied by the plate AB. However, the fundamental law which governs the motions of electrons on the classical theory is

the law that each electron moves in such a manner that

$$\iiint\left(\mathbf{E}+\frac{[\mathbf{vH}]}{c}\right)\rho d\tau=0, \quad . \quad . \quad . \quad . \quad (7)$$

where the integral is taken all over the electron and **E** and **H** refer to the resultant field *. Thus the left-hand side of (3) is really zero and is not at all representative of the quantity which we wish to associate with the "pressure on the plate AB." On the other hand, the quantity $\left\{\iiint\frac{[\mathbf{EH}]_x}{c}d\tau\right\}_0^{\mathrm{T}}$, regarded in its proper light as taken throughout the whole volume, departs very far from the behaviour implied in the foregoing demonstration, in which it was assumed not to increase sensibly with increase of T for large values of T. It is quite true that it would have this property if the vectors in it referred only to those associated with the plane wave; but, in the sense of the demonstration they refer to the *total* field, and the quantity in question includes, as part of itself, *the electromagnetic momentum imparted to the plate* AB *by the pressure*, which momentum would be evidenced in the motion of the plate if left to itself.

A Modified Derivation.

(1) *Case where the Plate is Allowed to Move under the Pressure.*—Let us separate the field at each point in space into two parts, the field $\mathbf{E}_0$, $\mathbf{H}_0$, of the primary wave, and the remainder $\mathbf{E}_i$, $\mathbf{H}_i$, which is really produced by the electronic motions in the plate and which manifests itself partly as the electromagnetic waves which cancel the incident wave to the right of AB, or constitute the reflected wave to the left, and partly as the increase of electromagnetic momentum of the plate AB. Thus, having in mind that the left-hand side of (3) is zero, we have,

$$0=-\left\{\iiint\frac{[\mathbf{E}_0+\mathbf{E}_i\,.\,\mathbf{H}_0+\mathbf{H}_i]_x}{c}d\tau\right\}_0^{\mathrm{T}}$$
$$-\int_0^{\mathrm{T}}dt\iint\frac{(\mathbf{E}^2+\mathrm{H}^2)}{2}d\mathrm{S}, \quad . \quad (8)$$

where the square bracket indicates a vector product as

* See H. A. Lorentz, 'Theory of Electrons,' p. 43.

Strictly speaking the law must be taken in the sense that, at each instant, the volume integral is referred to axes with respect to which the electron is momentarily at rest. However, the elements involved in this matter are not pertinent to the present discussion.

before, and where, in the surface integral, we have not dissected the field into the two parts corresponding to the subscripts i and 0.

Now suppose that, at $t=0$, the primary train of waves, which we shall suppose of limited extent, has just reached EF, and that at the end of the time T the tail of it has passed far to the right of GH, and any reflected part has passed far to the left of EF. Then, since at the beginning and end of the time T, $\mathbf{E}_0$ and $\mathbf{H}_0$ are zero, the value of the first term on the right-hand side of (8) is

$$-\text{Change of } \iiint \frac{[\mathbf{E}_i\mathbf{H}_i]_x}{c} d\tau \text{ during the time T.} \quad . \quad (9)$$

But since, by hypothesis, the tail of the primary wave has passed well to the right of GH at the end of the time T, and since the wave of cancellation has also passed well to the right of GH, and any reflected wave has passed well to the left of EF, expression (9) is left as the representative of the change of electromagnetic momentum of the fields of the electrons in the plate AB as a result of the passage of the train of waves.

As regards the second term on the right-hand side of (8) representing the time integral of $\frac{1}{2}(\mathbf{E}^2+\mathbf{H}^2)$ over the planes EF and HG, in the case of total absorption its value is zero over HG and *minus* the time integral of $\frac{1}{2}(\mathbf{E}_0^2+\mathbf{H}_0^2)d\mathrm{S}$ over EF. In the case of total reflexion it is again zero over GH but is equal to *minus* the time integral of $(\mathbf{E}_0^2+\mathbf{H}_0^2)d\mathrm{S}$ for the plane EF. Thus we have the conclusion that *if a train of plane waves falls upon a plate for a long time* T *and is absorbed, the electromagnetic momentum communicated to the plate is the same as that produced by a pressure equal to the energy per c.c. in the plane wave acting for the same time. For total reflexion the effective pressure is twice the above amount.* The line of proof for intermediate conditions is sufficiently obvious, and needs no comment.

The only reason for considering the transition from one steady state of motion of the plate to another which is attained after the radiation has passed completely, is to avoid the awkwardness of definition involved in saying how much of the electromagnetic momentum is to be assigned to the plate, and how much to the radiation field which the plate is continually emitting for the purpose of cancellation of the primary wave to the right or for the purpose of reflexion to the left. Moreover, the result we have calculated is the only one which could have any experimental interest in general for the case where the plate is allowed to move.

As regards the customary proofs, it may be remarked that the sense in which the left-hand side of (1), and so of (6), appears to be understood as representing a pressure on the plate implies that the fields **E** and **H** refer to the fields of the plane waves alone and have nothing to do with the fields produced by the electrons except in so far as they contribute to the waves. As such, however, the left-hand side in question would have no status in electromagnetic theory at all. It is true that equation (1) holds for every field which *in itself* constitutes a solution of the electromagnetic equations and not merely for the resultant field alone; but the equation is meaningless, or at best hopelessly wrong, unless applied to a situation in which the **E** of the left-hand side of (1) contains in its divergence the quantity ρ which also occurs in the integral. As a matter of fact the customary derivation endeavours to proceed without utilizing the force equation (7), which is the sole means of determining what happens to the plate dynamically. Equation (1) contains nothing but the circuital relations of electromagnetic theory plus pure algebra. The circuital relations themselves have nothing whatever to say about the motions of charges, so that to attempt to use their consequence (1) to evolve, without the aid of some additional assumption such as (7), an explanation of what happens as regards the motion of a plate upon which radiation falls is to attempt to get something out of nothing *.

(2) *Case where the Plate is Held Fixed.*—In the case where the plate is supposed held fixed by an external force the argument must take a different form. On the basis of an electromagnetic explanation of things it is necessary to regard the external force as ultimately of electromagnetic nature. For the purposes of a mental picture, we may suppose the plate to be charged, and in spite of the action of the radiation, held fixed through the influence of a statical electric field. For the purpose of the general discussion of the problem, however, no such detailed picture of the mechanism is necessary. The mathematics simply makes use of the fact that, through the combined action of electromagnetic agencies—the radiation and the "external force"—the plate somehow or other finds itself at rest, and it proceeds to discuss the consequences. Nevertheless, as a preliminary, we shall discuss the case where the external

* See W. F. G. Swann, Phil. Mag. ser. 6, xxiii. pp. 86–94 (1912). Also, W. F. G. Swann, "The Fundamentals of Electrodynamics" (Section 1 of Bulletin No. 24 of the National Research Council), pp. 27, 33, and pp. 38–40.

force is brought about by the operation of an external uniform field e_x on a charge of surface density σ which is supposed spread over the plate.

Equation (7), with **E** and **H** referring to the total field, holds, of course, as before. Thus, the left-hand side of (1) is zero, and the first term on the right-hand side is also zero, since a steady state is postulated, so that we are left with

$$\iint(lp_{xx}+mp_{yx}+np_{zx})d\mathrm{S}=0. \quad . \quad . \quad . \quad (10)$$

Since e_x is parallel to the x axis, the quantities E_y, E_z, H_y, H_z, still refer to the y and z components of the resultant field and also to the field of the wave, modified as it may be by absorption or reflexion.

The charge density σ gives rise to a uniform field $+\bar{e}_x$, to the right of the plate, and $-\bar{e}_x$ to the left, where $\bar{e}_x$ is given in Heavisidean units, by

$$\bar{e}_x=\tfrac{1}{2}\sigma. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Thus, since the field of the wave to the right of the plate is zero, the use of the expressions following (1) causes (10) to take the form

$$\{\mathrm{E}_y^2+\mathrm{E}_z^2+\mathrm{H}_y^2+\mathrm{H}_z^2+(e_x-\bar{e}_x)^2\}-\{e_x+\bar{e}_x\}^2=0, \quad (12)$$

the first expression on the left-hand side of (12) corresponding to the surface integral over one square centimetre of the plane EF and the second expression referring to the corresponding quantity for GH. Thus

$$\mathrm{E}_y^2+\mathrm{E}_z^2+\mathrm{H}_y^2+\mathrm{H}_z^2=4e_x\bar{e}_x,$$

so that, using (11),

$$\tfrac{1}{2}(\mathrm{E}_y^2+\mathrm{E}_z^2+\mathrm{H}_y^2+\mathrm{H}_z^2)=\sigma e_x. \quad . \quad . \quad . \quad (13)$$

For a case where there is no reflexion, the quantities E_y, E_z, H_y, H_z refer to the field of the incident wave, so that the left-hand side of (13) represents the energy per c.c. in the incident wave, while the right-hand side represents the electric force per unit area due to the equilibriating field; and the equality of these two as given by (13) expresses, in a rational and understandable way, the precise meaning of the result deduced. For the case of complete reflexion, the left-hand side of (13) corresponds to twice the energy per c.c. in the incident wave, and this is the quantity which, for this case, is equal to σe_x.

If we do not wish to limit ourselves to the simple case of an equilibriating field of a uniform type operating on a charge

density σ, but desire to leave open the question of just how the equilibriating force (produced by the hand, for example) is to be represented in electromagnetic fashion, subject only to the belief that it is capable of such representation, we proceed as follows :—

Again let us divide the total field into a part $\mathbf{E}_0$, $\mathbf{H}_0$, corresponding to the field of the incident wave and a remainder which we shall call $\mathbf{E}_k$, $\mathbf{H}_k$, since it is not quite the same thing as the field $\mathbf{E}_i$, $\mathbf{H}_i$, which was concerned when the plate was allowed to move, but includes the fields associated with the equilibriating forces. Applying our argument to a region corresponding to a square centimetre of the plate, equation (7) tells us that

$$\iiint\left(\mathbf{E}_0+\frac{[\mathbf{v}\mathbf{H}_0]}{c}\right)\rho d\tau+\iiint\left(\mathbf{E}_k+\frac{[\mathbf{v}\mathbf{H}_k]}{c}\right)\rho d\tau=0. \quad (14)$$

Now the field $\mathbf{E}_k$, $\mathbf{H}_k$, in conjunction with the charge density expressed by ρ, is a solution of the electromagnetic equations, for it is the difference between the total field $\mathbf{E}$, $\mathbf{H}$, which is, of course, a solution of the electromagnetic equations, and the field $\mathbf{E}_0$, $\mathbf{H}_0$, which is also a solution of the electromagnetic equations and has no singularities in the region considered. Thus equation (1) holds for the field $\mathbf{E}_k$, $\mathbf{H}_k$, taken by itself, and we have

$$-\iiint\left(\mathbf{E}_k+\frac{[\mathbf{v}\mathbf{H}_k]}{c}\right)_x\rho d\tau=\frac{\partial}{\partial t}\iiint\frac{[\mathbf{E}_k\mathbf{H}_k]_x}{c}d\tau$$
$$-\iint\left\{l(p_k)_{xx}+m(p_k)_{yx}+n(p_k)_{zx}\right\}d\mathrm{S}, \quad . \quad (15)$$

where the p_k's are defined as in the lines immediately following (1), but, of course, with the subscript k. The region of integration is, as before, that indicated in fig. 1.

Now the first term on the right-hand side of (15) is the rate of increase of the electromagnetic momentum of the field $\mathbf{E}_k$, $\mathbf{H}_k$, for the region indicated by EFHG, and this is zero since the plate is postulated to be at rest *. It is not the purpose of the analysis to inquire how it may come about that the plate can remain at rest, under the combined

* Strictly speaking we should speak throughout in terms of averages taken over a long time, which would permit of vibrations of the plate with the period of the light waves. The extension to this line of argument is simple and obvious, though rather cumbersome of expression, and we shall not complicate matters by considering it.

influence of the radiation and the external forces. The business of the analysis is to postulate it and trace its consequences. The first term on the right-hand side of (15) being thus zero, we are left with

$$\iiint\left(\mathbf{E}_0+\frac{[\mathbf{v}\mathbf{H}_0]}{c}\right)_x\rho d\tau = -\iint\left\{l(p_k)_{xx}+m(p_k)_{yx}+n(p_k)_{zx}\right\}dS. \quad (16)$$

Now if we assume that the surfaces designated by EF and GH are so far away from the plate that the sole representative of the field $\mathbf{E}_k$, $\mathbf{H}_k$, there, is a plane wave, we see that, for the case of complete absorption, the field $\mathbf{E}_k$, $\mathbf{H}_k$ cancels $\mathbf{E}_0$, $\mathbf{H}_0$ over GH, and is zero over EF. For this case, therefore,

$$\iiint\left(\mathbf{E}_0+\frac{[\mathbf{v}\mathbf{H}_0]}{c}\right)_x\rho d\tau = \tfrac{1}{2}\iint\left\{(\mathbf{E}_0)_y{}^2+(\mathbf{E}_0)_z{}^2+(\mathbf{H}_0)_y{}^2+(\mathbf{H}_0)_z{}^2\right\}dS. \quad (17)$$

For the case of total reflexion, the surface EF contributes an equal amount to the right-hand side of (17), so that the result is doubled.

Now the left-hand side of (17) is the quantity which, in the ordinary usage of the terms, represents the force which the *field of the incident wave represented by* $\mathbf{E}_0$, $\mathbf{H}_0$ exerts on unit area of the plate, while the right-hand side of (17) is, of course, the energy per c.c. in the incident wave, and it is the equality of these, for the case of absorption, or the corresponding equality with the omission of the half for the case of reflexion which is the result to which electromagnetic theory leads for the case where the plate is held fixed. The general procedure for cases intermediate between complete absorption and complete reflexion will be sufficiently obvious.

Cases where the Laws are Not Entirely Electromagnetic.

For this case, the fundamental equation of electronic motion (7) must be replaced by

$$\iiint\left(\mathbf{E}+\frac{[\mathbf{v}\mathbf{H}]}{c}\right)\rho d\tau+\mathbf{F}=0, \quad . \quad . \quad . \quad (18)$$

where $\mathbf{F}$ is a "force" of non-electromagnetic origin. By tracing through the steps of the demonstration immediately preceding, and remembering that (15) still holds, it will

readily be seen that the only effect of the addition of **F** is a replacement of the integral on the left-hand side of (17) by this integral plus the result obtained by integrating **F** over unit area of the plate. Thus the conclusion reached is that the force per unit area due to the field $\mathbf{E}_0$, $\mathbf{H}_0$ of the incident wave *plus* the force per unit area due to **F** is equal to the energy per c.c. in the incident wave for the case of complete absorption or twice that amount for complete reflexion. It will also readily be seen that, for the case where the plate is allowed to move, the conclusion reached is that, in the complete passage of a train of waves, the momentum gained per unit area of the plate is equal to the time integral of the energy per c.c. in the incident train for complete absorption or twice this amount for complete reflexion *minus*, *in each case*, the time integral of the contribution of **F** to unit area of the plate.

Sloane Laboratory,
Yale University.
August 14, 1925.

L. *The Variation of the Thermal Conductivity of Gases with Pressure. By* H. Gregory, *B.Sc., D.I.C., Ph.D., and* C. T. Archer, *B.Sc., A.R.C.S., D.I.C., Physics Department, Royal College of Science, S.W.* 7 *.

(1) *Introduction.*

ONE of the earliest consequences, first deduced by Maxwell, of the analysis of the Kinetic Theory of Gases, was that within limits the Thermal Conductivity of a Gas should be independent of the Pressure of the Gas.

The transfer of heat across a layer of a gas whose faces are maintained at different temperatures is effected by the migration of molecules possessing greater kinetic energy, the migration in the opposite direction from the colder layer not being in thermal compensation. Reduction of pressure lowers the molecular concentration but at the same time causes an increase in the free path of the molecule, the two effects being compensating and therefore not affecting the transfer of heat.

Stefan † claimed to have shown this to be true experimentally, but his method of so doing was not at all sensitive and in the light of modern scientific accuracy cannot be

* Communicated by the Authors.

† Stefan, *Journ. de Phys.* vol. ii. p. 147 (1873).

accepted as an accurate experimental investigation of the effect.

Generally speaking, the measurement of transfer of heat in a gas is effected by the immersion of a heated body in an enclosure dimensionally symmetrical with the body and surrounded by a thermostatic arrangement. The great disadvantage is that associated with such a system, convective losses of heat exist to a greater or less degree with the purely conductive losses, and one of the greatest difficulties is not only to disentangle these losses one from the other, but to design a system in which all convective losses are absent.

In any investigation of the change of conductivity with pressure it cannot be too strongly emphasized that for any method to be susceptible of accuracy and sensitivity two fundamental points must be kept strictly in view :—

(1) The maintenance at constant temperature of the heated body in the gas, and the arrangement for so doing must be sensitive and easily adjustable during the variation of the pressure conditions, and

(2) The troublesome elimination of the convective losses which vary considerably with the pressure.

If the constant temperature obligation can be accurately fulfilled, the investigation is considerably simplified. For, taking the example of a wire coaxial with a tube whose external surface is maintained at a constant temperature, and the wire heated by an electric current, it is obvious that if the pressure is lowered, in the absence of convection, we need only to consider the change in the current strength if the wire can be maintained at constant temperature. This not only simplifies the investigation, but enables the whole subject to be treated from the point of view of a qualitative test, while the results lose nothing in the accurate sense of the word. The partial failure of other observers in the subject is attributed to the fact that this important point has not been considered sufficiently.

(2) *Principle of the Method.*

The experiments of Todd *, and also those of Hercus and Laby †, involved an experimental system which was free from the complications of convective losses of heat. In the first case, although it would have been possible to maintain

* Todd, Proc. Roy. Soc. (83) p. 19 (1909).

† Hercus and Laby, *loc. cit.* (95), p. 190 (1918).

the hot body at constant temperature during the variation of the pressure conditions, it was not possible to measure any slight changes in the transmitted heat, which had been shown by Stefan to be small if any at all. In the second case, the disposition of emitting and receiving surfaces, similar to those of Todd, was capable of greater accuracy, and temperatures were measured by a potentiometer system. Such systems were not at all suitable for a test of the variation of conduction with pressure, and after experiments with plate systems, the authors came to the conclusion that the hot-wire method is infinitely superior, both from the point of view of convenience in designing such an apparatus and also by its much greater simplicity of detail and sensitivity. The one trouble with the hot-wire method is that it is difficult to eliminate convective losses of heat, but it has been found that such difficulties are not insuperable.

Weber *, making use of a vertical disposition of tubes in his hot-wire method, arranged the inlet tubes for the gas in the upper part of the experimental tubes, which necessarily made convective losses inherent in the apparatus, and his experimental system was such that he was unable to maintain the wire at constant temperature during the variation of pressure. The authors found by experiment that with a vertical disposition of tubes it is possible to minimise the convective losses.

It cannot be emphasized too strongly how important the maintenance of the wire at constant temperature is in an investigation of this nature. In the present case, this can be done to a high degree of accuracy, making it possible to base the whole effect of the change, if any, on a change in the current strength.

If reference is made to fig. 1, it will be seen that the elimination of the convective losses has been brought about by the observance of the following points :—

(1) Springs are fixed in the lower part of the tube to maintain the centrality of the wire, and since the temperature distribution here is from above to below no convective losses are possible on this account ;

(2) The thin wire is continued as far as possible into the closed upper end of the tube ;

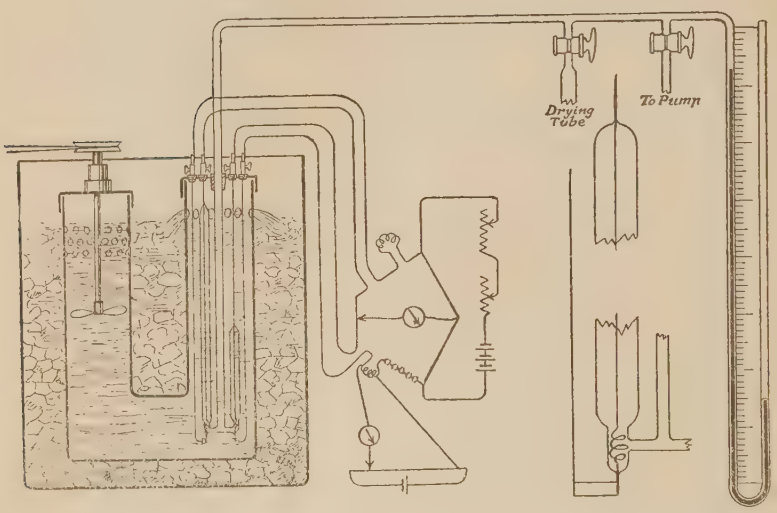
(3) The tube has been made as narrow as possible consistent with the accuracy demanded, again obviating convective loss, since it was found in our main research work that such loss increases rapidly with width of tube ;

* S. Weber, *Ann. der Phys.* vol. liv. p. 325 (1917).

(4) The use of very thin wire, diameter 0·004 inch approx.;

(5) The inlet tubes are at the lower end of the experimental tubes.

Fig. 1.



A main tube constructed on these lines and in conjunction with a similar compensating tube was mounted rigidly and vertically on a brass plate and the whole fixed in one arm of a large brass U-tube, through which a constant stream of water could be forced by means of a propeller worked by an electric motor.

(3) *Theory of the Method.*

The equation of heat transmission applicable to the above disposition of tubes, assuming that all convective losses are absent, is

$$C^2R = \frac{2\pi K\theta l}{\log_e r_2/r_1} + \phi,$$

where C denotes the current strength, R the resistance of the effective length l of thin wire in the main tube which is of uniform temperature θ° C. along its length, the end effects due to heat conducted along the leading wires being compensated by the shorter tube, a point which has been strictly dealt with in our main research; r_2 is the internal radius of the glass tube, and r_1 the radius of cross-section of

the platinum wire, ϕ being the heat loss due to radiation from the wire at the temperature θ° C.

If the temperature of the wire is maintained constant throughout the changes in the pressure of the gas, then ϕ and R will be also constant, and the change in the conductivity K, if any, will be indicated by a corresponding change in the value of the current strength necessary to maintain the temperature of the wire constant.

The whole investigation of this effect is therefore one of great simplicity, and demands only consideration of the sensitivity of the experimental system to detect and measure such changes if any occur.

(4) *Construction and Arrangement of Apparatus.*

The tubes used in the experimental system were of lead glass supplied by Messrs. J. Powell & Sons (Whitefriars), Ltd. A suitable length of uniform bore was carefully chosen and its dimensions were taken, the internal radius by weighing the quantity of mercury required to fill a known length, and the external radius by means of repeated readings with an accurate slide-callipers.

The thin platinum wire was also carefully chosen as uniform as possible, and its radius found by accurately weighing lengths of about 100 cm. Also the resistance per unit length at different temperatures of the same wire was measured, as in the case of the wire used in the main research work*. The necessary lengths were then cut and attached to the leading wires and springs, which were made of thick platinum wire, and the complete wires mounted in the tubes, extreme care being taken that the wires were central along the whole length of each tube.

The tubes were next mounted, as explained above, on a brass plate fitting in one arm of a large brass U-tube. This was made from brass tubing 3 inches in diameter, and in the other arm of the U was mounted a large motor-driven paddle-wheel. The whole arrangement was finally fixed rigidly in a galvanized iron tank of about 10 gallons capacity. A plentiful supply of ground ice and a moderately good speed of the paddle-wheel ensured that a copious stream of ice-cold water passed through the U-tube, maintaining the external surface of the experimental tubes at constant and uniform temperature, 0° C.

After mounting the tubes, the fundamental interval of the effective length of thin platinum wire was next carefully

* Gregory and Archer, Proc. Roy. Soc. cx. p. 91 (1926).

determined, using the temperatures of melting ice and of steam as the fixed points and the Callendar-Griffiths bridge.

The scheme of connexions for the electrical circuit is also shown in fig. 1. The main tube was connected in series with a standard 1 ohm resistance coil in the main arm of the Callendar-Griffiths bridge, which had been calibrated completely previously, and the compensating tube, also in series with a similar and equal standard resistance coil, in the compensating arm of the bridge. The current was supplied by a battery of 2 volt accumulators, and the measurement of the current was carried out by means of a potentiometer connected across the terminals of the standard resistance coil in the main arm of the bridge.

The dimensions, etc. of the apparatus are shown :—

Internal radius of tubes (r_2), 0·5144 cm.
External „ „ (r_3), 0·605 cm.
Radius of platinum wire (r_1), 0·005301 cm.
Resistance of wire at 0° C., 224·009 cm. bridge wire.
„ „ 100°·49 C., 311·365 „ „
Fundamental interval of wire between 0° C. and 100°·49 C., 87·356 cm. bridge wire.
$\log_e r_2/r_1$, 4·5751.
$\log_e r_3/r_2$, 0·1623.

(5) *Measurement of Current.*

As stated above, the whole experimental work was based on the detection and measurement of the changes of current required to maintain the wire at a constant temperature. For this purpose an accurate and carefully calibrated potentiometer made by the Cambridge and Paul Scientific Instrument Co., and of the "slide" type, was used. The scale of the slide wire was graduated so that 0·0001 ampere could be measured accurately. Changes of current smaller than 0·0001 ampere could be detected easily though not measured by this instrument, and for this reason use was made of the deflexions of the galvanometer in the bridge circuit to calculate the smaller changes, when they occurred, as indicated below. (See paragraph 7.)

(6) *Experimental Procedure.*

Briefly, the experimental procedure was as follows :—

The tubes were filled with atmospheric air freed from dust and carbon dioxide and dried by means of phosphorus

pentoxide, and the apparatus operative in maintaining constancy of the external temperature was allowed to circulate for about an hour before any observations were recorded. The bridge setting was fixed to correspond to some temperature previously decided upon, the current was switched on and varied in strength by means of the rheostats in the circuit until the galvanometer indicated a balance. After allowing time for the stationary state to be reached, the current was measured by means of the potentiometer and the pressure readings were taken. The pressure of the gas was then reduced by about 10 cm. of mercury and, after a short interval of time, a test was made to find whether any change in the current strength was necessary to fit in with the new condition of pressure.

An important point at this stage is to decide how far such changes, if any, are due to a possible change in the conductivity or to other variable effects existing in the experimental system. This point has been considered fully below.

The pressure was lowered in this manner in stages of about 10 cm. of mercury and the corresponding current was measured.

After a certain pressure, the mean free path, becoming greater as the pressure of the gas is reduced, begins to approach a value comparable with the distance between the wire and the internal surface of the tube, and there should be at this stage a change in the conductivity due to this effect. This is shown up beautifully in the existing experimental system, the effect occurring in a very gradual manner at first and then, as the pressure is further reduced, in a more marked degree, and at a pressure of about 0·5 cm. (a pressure which depends upon the dimensions of the tubes) undergoes a considerable change.

It is important to notice here that the sensitivity of the experimental system was such that great precautions were necessary to maintain the taps etc. perfectly gas-tight, owing to the rapid change of $d\mathrm{K}/dp$.

It might also be pointed out that the changes in the conductivity with pressure at very low pressures could be followed easily by the arrangement described, but a difficulty is met with in the fact that it is difficult to measure small pressures with any degree of accuracy, and consequently such observations would be valueless. Though such observations have not been carried out in the present case, arrangements are under consideration, however, to carry out this research separately.

Observations were taken with the wire at different

temperatures, and the results are embodied in the series of tables given below, from which the curves shown in fig. 2

Fig. 2.

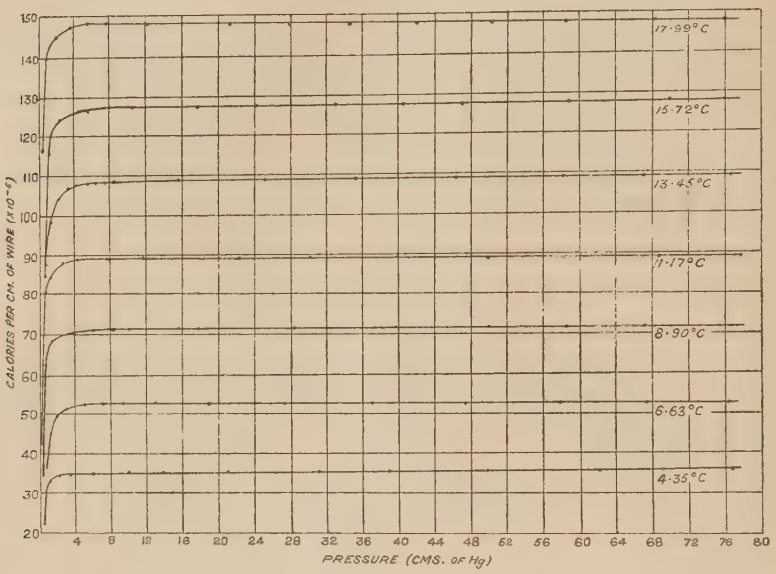


TABLE I.

Temperature of wire, 17°·990 C.
R/*l* at 17°·990 C. 0·12460 ohm.

p.	C.	W.
76·94	0·2234	0·0014861
68·21	,,	,,
58·97	,,	,,
50·16	,,	,,
42·05	,,	,,
34·72	,,	,,
27·99	,,	,,
21·59	0·2232	0·0014835
12·19	0·2229	0·0014794
7·67	0·2227	0·0014768
5·73	0·2225	0·0014742
3·63	0·2220	0·0014676
1·75	0·2205	0·0014478
0·79	0·2167	0·0013984
0·29	0·1975	0·0011616

have been obtained by plotting the values of the total heat loss at various pressures calculated from the experimental results. The tables are made up of (1) the pressure in cm. of mercury, (2) the current strength in amperes, (3) the total heat loss per cm. of wire calculated from the current

TABLE II.

Temperature of wire, 15°·717 C.
R/l at 15°·717 C., 0·12356 ohm.

p.	C.	W.
76·89	0·2084	0·0012826
70·29	,,	,,
62·19	,,	,,
54·97	,,	,,
47·58	,,	,,
40·40	,,	,,
32·92	0·2083	0·0012814
24·01	0·2082	0·0012802
17·72	0·2080	0·0012776
10·45	0·2077	0·0012740
5·40	0·2073	0·0012692
2·24	0·2060	0·0012503
0·60	0·1978	0·0011555
0·28	0·1688	0·0008415

TABLE III.

Temperature of wire, 13°·445 C.
R/l at 13°·445 C. 0·12252 ohm.

p.	C.	W.
76·79	0·1921	0·0010805
67·24	,,	,,
58·04	,,	,,
46·16	,,	,,
35·36	,,	,,
25·22	0·1920	0·0010794
15·79	0·1919	0·0010783
8·22	0·1918	0·0010771
7·56	0·1916	0·0010749
6·52	0·1914	0·0010726
5·26	0·1912	0·0010703
4·04	0·1910	0·0010682
2·86	0·1906	0·0010636
1·54	0·1894	0·0010504
1·02	0·1880	0·0010349
0·44	0·1837	0·0009882
0·22	0·1727	0·0008733

strength and the resistance per cm. of wire at the appropriate temperature, taking $J = 4{\cdot}184$. The temperature of the wire and the resistance per unit length of wire at this temperature are shown at the head of each table.

TABLE IV.

Temperature of wire, 11°·171 C.
R/l at 11°·171 C., 0·12148 ohm.

p.	C.	W.
77·61	0·1756	0·00089518
68·49	,,	,,
57·93	,,	,,
49·67	,,	,,
39·84	,,	,,
30·55	,,	,,
22·61	,,	,,
11·77	0·1755	0·00089414
9·51	,,	,,
7·59	0·1754	0·00089316
4·31	0·1750	0·00088911
2·17	0·1742	0·00088102
1·07	0·1726	0·00086488
0·45	0·1663	0·00080290
0·25	0·1207	0·00042286

TABLE V.

Temperature of wire, 8°·898 C.
R/l at 8°·898 C., 0·12044 ohm.

p.	C.	W.
77·59	0·1575	0·00071399
68·01	,,	,,
58·72	,,	,,
49·89	,,	,,
40·26	,,	,,
28·14	,,	,,
17·69	,,	,,
14·13	0·1574	0·00071307
9·93	,,	,,
8·03	0·1573	0·00071219
5·97	0·1571	0·00071039
4·03	0·1568	0·00070760
1·97	0·1560	0·00070043
0·77	0·1539	0·00068177
0·33	0·1482	0·00063218
0·09	0·1088	0·00034075

TABLE VI.

Temperature of wire, 6°·626 C.
R/*l* at 6°·626 C., 0·11940 ohm.

p.	C.	W.
76·56	0·1372	0·00053717
67·46	,,	,,
57·46	,,	,,
47·61	,,	,,
36·81	,,	,,
27·25	,,	,,
17·15	,,	,,
12·75	0·1371	0·00053640
11·03	0·1370	0·00053560
9·19	0·1369	0·00053477
7·01	0·1368	0·00053400
5·05	0·1366	0·00053246
3·15	0·1363	0·00053014
1·43	0·1345	0·00051630
0·63	0·1261	0·00045376
0·33	0·1119	0·00035727

TABLE VII.

Temperature of wire, 4°·352 C.
R/*l* at 4°·352 C., 0·11836 ohm.

p.	C.	W.
76·67	0·1135	0·00036446
68·84	,,	,,
61·39	,,	,,
49·76	,,	,,
38·97	,,	,,
31·20	,,	,,
20·83	,,	,,
13·54	0·1134	0·00036381
9·17	0·1132	0·00036251
5·97	0·1129	0·00036060
3·13	0·1126	0·00035868
1·79	0·1120	0·00035486
0·79	0·1101	0·00034288
0·37	0·1036	0·00030366
0·23	0·0888	0·00022306

(7) *Absolute Determination of the Conductivity.*

Although it is not claimed that the present investigation is an absolute determination of the thermal conductivity, the conductivity has been calculated from the experimental data and measurements of the dimensions of the tubes and wire, taking the figures shown in Table II., and, as will be seen, differs by less than 1 per cent. from the value of K arrived at in the more accurate main research on the conductivity of atmospheric air. The values are shown in Table VIII. The small difference is explained by the fact that in the present case the dimensions of the tubes and wire were chosen with a strict view to the elimination of convection, and these dimensions, especially of the wire whose diameter was about 0·004 inch as against 0·006 inch, were not susceptible of the same accuracy of measurement as in the case of those in the main research.

The quantities shown in Table VIII. are (1) the total heat loss per cm. of wire taken from Table II., (2) the total heat loss per cm. of wire after allowing for the loss by radiation, (3) the temperature drop across the glass wall of the tube, calculated as in the main research, (4) the gradient of temperature between the wire and the inner surface of the tube, (5) the actual deflexion of the galvanometer on changing the pressure of the gas, (6) the value of the thermal conductivity calculated from the observations given, and (7) the apparent effect on the conductivity produced by change of pressure, calculated as indicated below.

With reference to columns (5) and (7), it was found during the experiments that on changing the pressure of the gas small deflexions of the galvanometer of the order of 10 scale divisions occurred, indicating that current changes were required, though such changes were too small to be measured by the potentiometer. On this account it was thought necessary to investigate the effect of such changes on the heat transmission. For this purpose the galvanometer deflexions were recorded as shown, and a separate experiment was made to determine the current sensitivity of the bridge system. Repeated observations showed that to produce a galvanometer deflexion of 1 scale division a change of current of 0·000002 ampere was required. Using this value with the deflexions recorded the changes of current were calculated, and thence the effect on the conductivity in each case was found by using the relation

$$\delta K = K \times \frac{2\delta C}{C},$$

where δC is the change of current calculated and C the current used and measured by the potentiometer.

As the deflexions were sometimes to the right and sometimes to the left, we have considered such changes to be indicative of some change of other conditions existing in the experimental system and not due to any change in the conductivity. Such a change might easily be brought about by a temporary aberration in the constancy of the external temperature, a variation in this temperature of even 0°·001 C. being capable of producing such a deflexion of the galvanometer.

It will be seen from the Table that the effect on K of these small changes is in the fourth and fifth significant figures only.

TABLE VIII.

W.	W′.	θ'.	θ.		K.	δ K.
0·0012826	0·0012748	0·020	15·697	3 div. right	0·00005914	$+34\times10^{-10}$
,,	,,	,,	,,	5 ,,	,,	$+57\times10^{-10}$
,,	,,	,,	,,	0	,,	
,,	,,	,,	,,	10 div. left	,,	-114×10^{-10}
,,	,,	,,	,,	2 div. right	,,	$+23\times10^{-10}$
,,	,,	,,	,,		,,	
0·0012814	0·0012736	,,	,,		0·00005908	
0·0012802	0·0012724	,,	,,		0·00005903	
0·0012776	0·0012698	,,	,,		0·00005890	
0·0012740	0·0012662	,,	,,		0·00005874	
0·0012692	0·0012614	,,	,,		0·00005852	
0·0012503	0·0012425	0·019	15·698		0·00005764	
0·0011555	0·0011477	0·018	15·699		0·00005324	
0·0008415	0·0008337	0·013	15·704		0·00003866	

(8) *Conclusion.*

The results of the preceding investigation indicate that, assuming convective losses to be absent, Maxwell's theoretical

prediction of the non-variation of thermal conductivity with pressure is true to the order of accuracy claimed in the experimental work.

With regard to higher pressures, the authors propose to extend the experiments to involve the use of pressures higher than that of the atmosphere.

LI. *On the Nature of the "Critical Increment" of Chemical Action.* *By* T. Carlton Sutton, *M.Sc., F.Inst.P.**

A NUMBER of problems may be attacked by means of either thermodynamics or the kinetic theory, the results obtained by each method being in good agreement with experiment and with one another.

Although hitherto more has been done by means of the thermodynamic than the kinetic method, the latter has supplied information on a number of points which are left indeterminate by the former.

It is the object of the present note to point out that some views recently put forward by Garner† are confirmed when examined from the kinetic view-point, and to indicate that values obtained for the constants in Garner's equations give information of use in the further development of the kinetic theory.

Garner puts forward the view that when two "active" molecules collide, alteration in their chemical nature need not necessarily result, and that there is no reason why a collision between active molecules should not sometimes result in the reformation of the actual reactants, instead of the formation of new compounds as resultants of the collision.

Hinshelwood‡ contends that this is not so, and that whenever the proportion of collisions which result in chemical action (in the ordinary sense of producing other compounds as resultants) is measured it is found to approach unity. This is based on the view that all "activated" molecules have the same energy, and on experimental data obtained from examination of the three reactions§ $2HI = H_2 + I_2$, $2N_2O = 2N_2 + O_2$, and $2Cl_2O = 2Cl_2 + O_2$.

Since the assumption of similar energy can be challenged, and the accuracy§ of the experimental measurements is

* Communicated by the Author.

† Garner, Phil. Mag. xlix. p. 463 (1925).

‡ Hinshelwood, Phil. Mag. l. p. 360 (1925).

§ Garner, Phil. Mag. l. p. 1031 (1925).

insufficient for the purpose, his case must be regarded as unproven.

It is here that the view-point of the kinetic theory is of service.

As long ago as 1914, the present author * (among others) examined the mechanism in accordance with which some molecules behave as "activated" molecules while others do not. A rigid mathematical derivation was then given of the view now generally accepted (quoted in a specialized form by Hinshelwood) that "activated molecules are molecules with specified energies." How many of these exist, and how many collisions take place between them, is determined by the temperature. Measurements to date confirm that the numbers both (i.) of molecules with specified energy and (ii.) of collisions, are in accord with these mathematically derived results and follow classical Maxwellian distribution.

The velocity of a monomolecular† action increases with temperature in a way similar to that of bimolecular actions‡. This fact is used in the paper of 1914 (p. 805) to show that the rotational velocities of the molecules and the velocity of any atom in the molecule (relative to the velocity of the molecule as a whole) accord with the Maxwellian distribution also.

The rotational and internal energy of the molecule must necessarily play a critical role in determining :—

(i.) whether a collision does or does not cause disruption ; and

(ii.) whether, once disruption is caused, combination takes place so as to reform the original reactants, or so as to form other compounds as resultants of the collision.

"Activated" molecules have sometimes been defined as those having a specified energy of translation, and sometimes as those having a specified total energy on impact. Further conditions may be imagined also, for instance there

* Sutton "On the Mechanism of Molecular Action", Phil. Mag. xxviii. p. 798 (1914).

† Hurst and Rideal, "Nitrogen Pentoxide" P. R. S. 109 A. p. 526 (1925). Hunt and Daniels, "Nitrogen Pentoxide," J. A. C. S. xlvii. p. 1602 (1925).

‡ *E. g.*, exponentially as indicated by the Maxwellian distribution. On the other hand, the rate of decomposition of the actual atoms of radioactive elements is independent of temperature. This may be used to show, by means of the kinetic argument, that the component parts of an atom do not move freely in their orbits and that their velocities do not accord with a Maxwellian distribution, a fact which agrees with the recent views of Lorenz and of Millikan.

may be molecules of high rotational energy on the point of centrifugal disruption.

Whatever view may be taken with respect to this, kinetic considerations show that when activated molecules collide, even if they approach in the actual line of centres, their energy distribution is by no means fixed ; there will be some collisions with translation energy suitable for reaction but with rotational and internal molecular energy unsuitable, and, likewise, some collisions with suitable internal, but unsuitable translational, energy. In fact there must be many collisions between these so-called "activated" molecules, which do not result in the formation of new chemical entities, that is to say in chemical interaction in the ordinary sense.

This is substantially the view which Garner has put forward on other grounds.

[It may be contested that "activated" molecules are actually defined as those which do interact on collision. This is a question of words. It is better merely to remark that "activated" is a word that has been inadequately defined, and to point out that in all probability the criterion determining reaction on collision is neither critical translational, nor rotational, nor internal molecular energy, nor that the sum of these energies should exceed a critical value ; the function of these three energies which must equal or exceed some critical value would appear to be more complex and has not as yet been determined.]

A relation between the velocities of the molecules and the velocities of the atoms in the molecules has already been derived *. Consequently when (with any appropriate definition of "activated") Garner has determined the proportion of collisions that react, *i. e.* his ratio $kc/(kc-kb)$, some idea will be gained of the absolute value of those velocities of the atoms within the molecule which are favourable to reaction. Correlation will then be possible with the sizes of the atomic orbits, the period of complete rotation of these orbits, and some of the absorption bands of the substance, especially those in the infra-red.

The author regrets that he has no opportunity of pursuing a research on these lines.

* Sutton, *loc. cit.*

LII. *The Emission of Electrons under the Influence of Intense Electric Fields.* *By* The Research Staff of the General Electric Co., Ltd.* (*Work conducted by* B. S. Gossling.)

[Received October 22, 1925.]

Abstract.

This paper is primarily an account of experiments on discharge currents observed in well-exhausted tubes and ascribable to the emission of electrons from metal surfaces under the influence of intense external electric fields, *cf.* Lilienfeld's autelectronic discharge.

A general description of the phenomena and in particular of the conditions under which definite numerical data can be obtained is first given.

The numerical data are then collected under the following heads :—

(*a*) The rapid continuous variation of the current (10^{-9} to 10^{-2} amp.) with the applied voltage and the connexion of these variables by a simple empirical relation.

(*b*) The nature of the discontinuous irregularities of the discharge.

(*c*) The influence of sodium and similar substances on these irregularities.

(*d*) The small and generally negligible effect of the temperature of the cathode (300° K. to 1700° K.).

(*e*) Minimum estimates of the current density (10^6 amps/cm.^{2}) and of the surface field (5×10^5 to 5×10^6 volts/cm.).

(*f*) The gradient of the current/voltage relation.

Schottky's theory of the autelectronic discharge is then briefly examined in the light of the measurements, and the general conclusion is reached that while the numerical data are not necessarily inconsistent with the fundamental assumption of the theory the question of the actual mechanism of emission is best left open, particularly since the data are definitely inconsistent with any simple application of the theory of thermionics.

---

(1) DISCHARGE currents of considerable strength, usually several milliamperes, have been obtained by Lilienfeld †‡ in high-vacuum X-ray tubes, using as the cathode a metal electrode provided with sharp points or edges.

These currents, since they were dependent rather on the form of the cathode and on its distance from the anode than

* Communicated by the Director.

† *Phys. Ber.* ii. p. 1350 (1921).

‡ *Phys. Zeit.* xxiii. p. 506 (1922).

on its temperature or on the degree of evacuation of the tube, were ascribed to the direct action of the applied field on the strongly curved portions of the cathode surface.

The emission of X-rays from the anode was localized in a few sharply defined areas, and there was evidence of emission of softer X-rays similarly localized on the points or edges of the cathode. It was inferred that the discharge took the form of a number of very fine pencils of cathode rays.

The voltage usually employed was 30,000 volts or more, but the discharge could be made to begin at much lower voltages dependent on the material of the cathode, for heavy metals about 5000 volts, and for a caesium cathode a few hundred volts.

Experiments aiming at the proof or disproof of the existence of a critical value of the surface field necessary for the passage of a discharge between metal electrodes in vacuum using high voltages have also been described by Millikan and Shackelford * †, and by Hayden ‡, while Rother § and Hofmann ‖ have recently made similar determinations, using moderate voltages and minute gaps between the electrodes.

The conditions under which electrons may be expected to be liberated from the surface of a metallic conductor under the attraction of a strong external field have been discussed in general terms by Schottky in a review of the subject ¶, in which he attempts to correlate a large number of phenomena.

Schottky's theoretical treatment is admittedly incomplete owing to lack of suitable experimental evidence; accordingly an account of some further experiments made under conditions analogous to those of Lilienfeld's autelectronic discharge may be useful. These, while they appear to confirm in general the observations of Lilienfeld, throw light on some features on which he has not touched.

(2) *Early Observations.*

Since the investigations to be described are chiefly experimental, a general account of the phenomena as we have observed them will first be given.

* Phys. Rev. xii. p. 167 (1918).
† Phys. Rev. xv. p. 239 (1920).
‡ Jour. Am. I. E. E. xli. p. 852 (1922).
§ *Phys. Zeit.* xxiii. p. 423 (1922).
‖ *Zeit. f. Phys.* iv. p. 363 (1921).
¶ *Zeit. f. Phys.* xiv. p. 63 (1923).

Unsupported discharge currents can be produced in any type of well-exhausted thermionic valve without any heating of the filament, provided that a sufficiently high voltage can be applied between the electrodes of the valve without external sparking between the connecting wires. Usually, however, these currents are of an extremely transitory nature ; all that can be seen is a flash of fluorescence of the walls of the exhausted bulb, with perhaps a few brilliant white scintillations on the surface of the electrodes, a throw of the pointer of the current indicating instrument, if this is not too sluggish, and, not infrequently, sparking and other forms of breakdown in the high voltage supply circuits. These breakdowns are usually such as require a considerable excess voltage, and therefore indicate that the discharge current was of considerable magnitude and very short duration. The discharges tend to be rather more violent when the cathode filament is cold than when it is incandescent.

In this transitory form the phenomena, though they may become very familiar, do not lend themselves to investigation.

If, however, the valve is first well exhausted, the electrodes being heated either by relatively low voltage thermionic bombardment or by high-frequency induction currents, and if the high voltage is applied through a resistance of the order of a megohm the discharge lasts much longer, often for several minutes, and the main effects can be more closely observed.

These are briefly as follows :—

(*a*) If the current is strong enough, currents of several milliamperes being readily obtained, the positive electrode is heated.

(*b*) This heating may be extremely local but very intense, *e. g.* holes of diameter one or two millimetres may be melted in a nickel sheet.

(*c*) The fluorescence of the glass is also localized in sharply defined patches, representing sections of cones of vertical angle often less than 10°.

(*d*) The fluorescent patches may be crossed by sharp shadows of the electrodes and their supports.

(*e*) There are local patches of coloured luminescence on the surface of the positive electrode similar in shape to the fluorescent patches on the glass, but succeeded by local heating if the current is maintained at sufficient strength.

(*f*) The hot spots on the anode are most frequent where the distance from anode to cathode is smallest, and their occurrence is particularly favoured by points or sharp edges projecting from the cathode.

(*g*) The current changes from one value to another at irregular intervals, but clearly increases rapidly with the applied voltage.

(*h*) The residual gas in the bulb plays at most a subsidiary part. The better the vacuum the less rapid the variations of the discharge current.

These phenomena are consistent with the supposition of a local emission of electrons from those parts of the cathode system, where the field at the surface is strong; such an emission may thus be a common occurrence given favourable conditions.

(3) *The Form of the Cathode and other Factors.*

The conditions governing this emission and the nature of various disturbing factors, the operation of which must be defined before theoretical discussion of the results is attempted, were investigated using discharge tubes of various forms; the main types are shown in fig. 1.

Fig. 1.

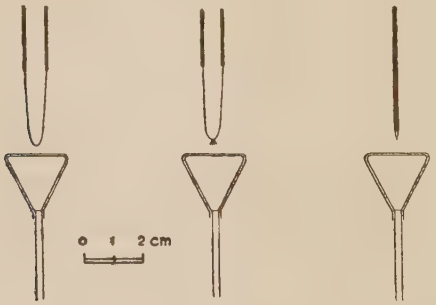


Fig. 1*a*. Loop filament.

Fig. 1*b*. Loop filament with brush.

Fig. 1*c*. Single end of wire.

The anodes in these tubes were disks 2 cm. in diameter, usually of nickel; with heavy discharge currents, however, even tungsten was readily melted. The distance between cathode and anode at the nearest point was about 0·3 cm.; the electrostatic field due to the anode would thus at this point approximate to that due to an infinite plane.

Comparison of the general behaviour of these tubes

showed that the form of the cathode is of the first importance. Thus, loop filaments of tungsten wire, ·02 cm. diameter, gave only transitory indications of discharge even with 60,000 volts between cathode and anode; whereas loops of finer wire, ·0015 cm. in diameter, never required more than 25,000 volts for a regular steady discharge. It is important to note, however, that the heating and luminescence of the anode obtained with a loop cathode was always just as strictly local as with pointed cathodes. There was no evidence of a general discharge from all parts of the surface of the wire. The addition of a brush of fine wires of ·002 cm. diameter to the thicker loop filaments never failed to produce discharge currents of the order of 1 milliampere at about 20,000 volts. A single end of ·002 cm. wire gave as heavy a discharge as a brush of 50 ends. Very fine points made by etching down the ·002 cm. wire to about ·0002 cm. (using the wire as anode in electrolysis of ammonia) never required more than 7000 to 10,000 volts for the same heavy discharge.

With a single point cathode the local heating or luminescence of the anode occurred now in one place and now in another, and occasionally in several places simultaneously.

Whatever the form of cathode employed, a general tendency for the discharge to take the form of a single pencil of small vertical angle was always observed.

Changes in the discharge current directly consequent on changes in the cathode temperature were found to be quite small in all these cases. Further observations on this effect will be considered in a later section of this paper.

No very marked differences in the discharge phenomena were observed when the preliminary exhaust by thermionic bombardment of the anode was omitted or left incomplete so that gas could accumulate during the passage of the discharge. At a pressure of ·0007 mm. white scintillations on the cathode and changes in position of the hot spot on the anode were frequent.

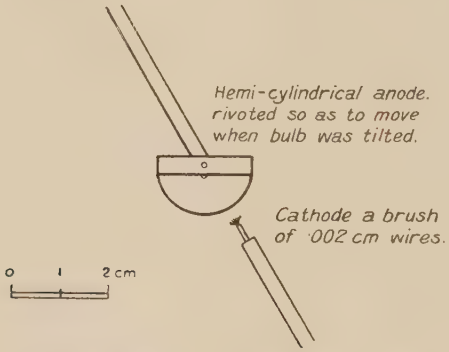
The question whether the anode played any part in the production of the discharge other than that of producing a strong field at the surface of the cathode was investigated by means of a tube having a cylindrical anode, fig. 2, pivoted so that by suitably inclining the bulb different parts of the anode surface could be presented to the cathode. It was found that as the cathode, which consisted of a brush of fine wires, passed over the surface of the anode the hot spot on the anode moved with it, and the discharge current was very little changed. After the tube had been in use some time

the current remained very nearly the same however the anode was moved.

It appears, therefore, that though the effects produced by the discharge on the anode are localized, no special condition occurring locally on the anode surface is a necessary condition of the discharge.

When the current was insufficient to produce a hot spot the corresponding luminescent area on the anode could be observed. This also followed the motion of the cathode, and although the luminescence might change the discharge current did not. Like the hot spot the luminescence is thus a secondary effect. It was observed that melting the anode surface by a heavy discharge destroyed the luminescence of the part melted.

Fig. 2.



Impact of the discharge on the glass gives fluorescence; many cases in which one part of a pencil of discharge strikes the anode, and the remainder the glass, have been observed.

With an open construction, such as a plate anode facing the cathode at two or three millimetres distance, the discharge does not necessarily pass direct to the anode but often by way of secondary emission of some sort from the glass. This may or may not heat the anode; there was a case when the tilting anode became hot on the opposite side from that at which the brush was presented. Again, very often, an ample current with much fluorescence of the glass and no luminescent patches on the anode has failed to produce visible red heat, when a change to smaller current with a luminescent patch and no fluorescence has produced intense heating.

The visible phenomena accompanying the discharge are thus very varied and tend often to obscure rather than reveal its nature. The way in which the current varies with the voltage is, however, absolutely characteristic of this type

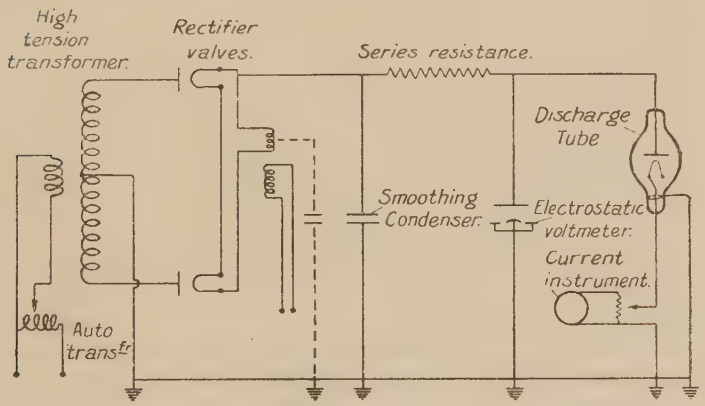
of discharge and enables it to be at once distinguished from any type of gas discharge. When the high voltage is first applied the discharge may set in suddenly with the accompaniment of a scintillation at the cathode. Its subsequent behaviour is, however, much more orderly. The range of variation of the currents observed has been from 10^{-9} ampere to about 5×10^{-3} ampere. Currents of 10^{-2} ampere and more can be obtained, but the melting of the anode and the likelihood of permanent changes at the cathode make continuous observation difficult.

From the lowest values up to about 10^{-4} ampere, the current varies very rapidly with the voltage. If the conditions are steady, as explained later, this variation is perfectly continuous and readings can be repeated whether the voltage is being raised or lowered.

(4) *Experimental Arrangements.*

Before we can consider the numerical data a brief description of the various circuit arrangements is necessary (fig. 3).

Fig. 3.



High tension supply circuit etc., using rectified alternating current.

In order to be sure of producing the full field at the surface of the cathode it would perhaps be better to have this electrode at a high negative potential and the anode at earth potential. For reasons of convenience the reverse arrangement was actually that generally adopted. When, however, with any particular tube, a change from the one arrangement to the other was made, there was never any marked change in the discharge current. It may therefore be concluded that the mere difference of potential of the two electrodes sufficiently defines the discharge conditions without reference to other bodies.

In all cases where the smaller currents were being observed the measuring instrument was placed between the low potential terminal of the tube and earth, and for the lowest currents, 10^{-9} ampere or so, an earthed guard-ring round the outside of the bulb near the low potential terminal was used. In any case leakage currents vary so slowly with the voltage that they can only affect the very first readings of any series.

The usual source of high potential was a 50 cycle alternating current transformer with a connexion to the centre point of the secondary winding acting as the negative output terminal. The high tension output terminal was connected to the filaments of two thermionic rectifier valves, the anodes of which were connected one to one end of the secondary winding of the transformer and the other to the other end. The potential between the output terminals thus tended to pulsate sinusoidally at the rate of 100 pulsations per second. A condenser connected across the output terminals eliminated these pulsations provided the output current was not excessive, that is, in the present case, did not much exceed 10^{-4} ampere. For these lower currents the numerical data obtained do not require correction and have therefore a much higher degree of certainty than those for currents of higher value. The effect of the necessary corrections on the data for the higher currents will be further discussed later.

The voltage adjustment was obtained by means of an auto-transformer with numerous tappings ; this had the advantage, particularly in the earlier experiments where the time element was important, of making possible a very rapid repetition of a definite series of voltages, without the temptation to dally over intermediate steps. At the lower voltages the steps of voltage were too large, but here it has since been possible to repeat some series of readings using a direct-current dynamo, and it is found that the more closely spaced intermediate readings so obtained agree well with the scattered readings of the previous observations.

The protecting resistances connected between the discharge tube and the high potential supply had values between 1 and 10 megohms, and consisted of glass tubes containing a saturated solution of copper sulphate crystals in glycerine *.

In plotting curves allowance is made for the voltage drop in the resistance When the resistance is in circuit a quick reading electrostatic voltmeter, connected across the discharge tube, affords useful evidence of the steadiness or otherwise of the discharge.

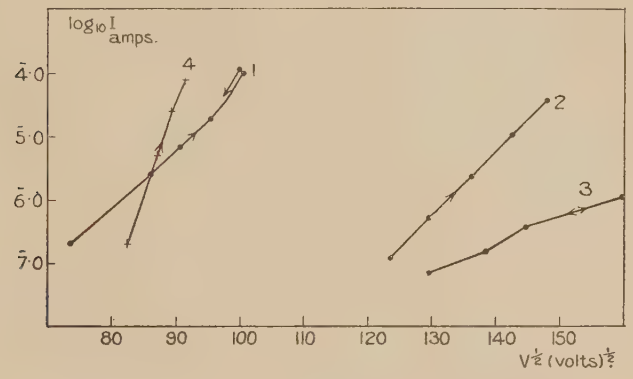
* A. Gilmour, Phil. Mag. xli. p. 544 (1921).

The currents given are in all cases the arithmetic mean values as indicated by a moving-coil instrument.

(5) *The Relation between Current and Voltage.*

In plotting numerical results the logarithm of the current is taken as ordinate and the square-root of the voltage as abscissa. Our reasons for the adoption of this method of plotting will appear when we come to the theoretical discussion of our results.

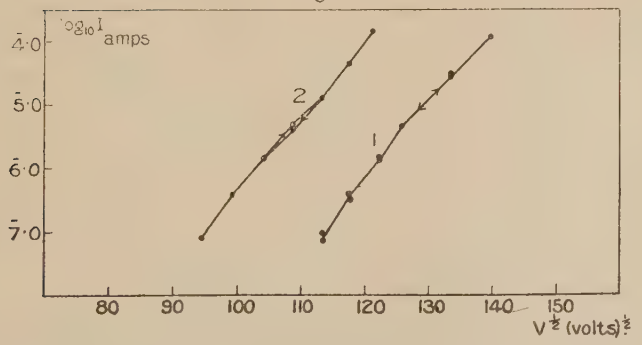
Fig. 4.



Cathode a loop of ·0016 cm. wire—electrostatic voltmeter.

Curve 1. First steady readings, before heating.
2. After heating by auxiliary current to 2300° K.
3. After further heating by auxiliary current to 2300° K.
4. After fracture of loop.

Fig. 5.



Cathodes—Curve 1 a single rounded point of ·002 cm. wire.
Curve 2 a brush of ·002 cm. wires.

Voltages from transformer peak (1·41 × R.M.S. value); series resistance 1·7 megohm.

This method of plotting proves illuminating as regards the initial stages of the discharge. Figures 4 and 5, showing

variations of current and voltage for various forms of cathode, indicate that the law of the discharge approximates, in the steady state represented by the cases selected, to the relation :—

$$I = Ae^{pV^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The range of variation of V is not, however, sufficient to determine accurately the power of V.

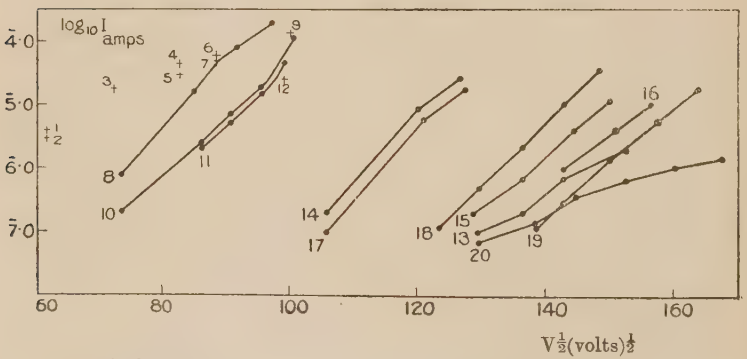
The coefficient p in the equation, *i.e.* $\frac{d \log_e I}{dV^{\frac{1}{2}}}$ is proportional to the gradient of the curves shown.

It appears from these curves, supported by a very much larger number of rather less reliable observations, that a current/voltage relation of this form holds generally from a current value of rather over 10^{-4} ampere down to the limit of observation ; a range in the case of the present experiments of 200,000 to 1 in current.

(6) *Discontinuous Irregularities of the Discharge.*

The existence of so simple an underlying relation makes it all the more necessary that an explanation should be

Fig. 6.



Cathode a loop of ·0016 cm. wire—electrostatic voltmeter.

found for the discrepancies and discontinuities which are so liable to occur among the numerical data. The same method of plotting is found to throw light on the nature of these irregularities of the discharge.

Figure 6 represents a series of characteristic curves taken

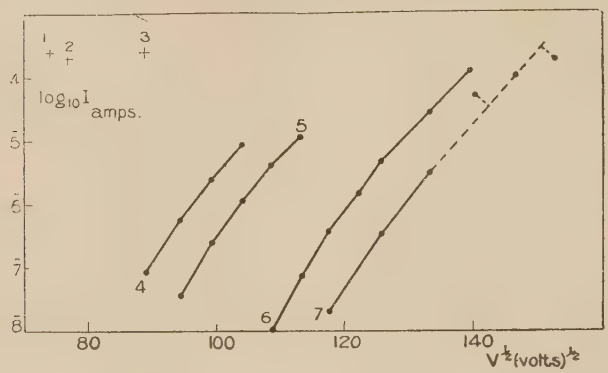
during the life-history of a particular tube. The various points and curves shown are numbered in chronological order. The anode in this tube had been heated during the exhaustion process by high frequency induction currents. The filament, a tungsten wire ·0016 cm. diameter, had no current passed through it at any time until the interval between curves 10 and 11. At first spontaneous changes—*e.g.* points 1 and 2, 4 and 5, 6 and 7—were frequent and only single points were obtained; the first definite curve was curve 8. The change from this to point 9 is typical of the effect of an over-rapid increase of voltage at this stage. The resulting new curve 10 is roughly parallel to its predecessor curve 8. The changes between curves 10 and 11 and most of the subsequent changes were induced by heating the filament, each time to a higher temperature; some of the changes were, however, spontaneous. The primary object of the experiments with this tube was to observe the effects of temperature such as will be discussed in a later section of this paper. The room temperature curves here shown illustrate very well the tendency of a given cathode to yield families of curves having approximately the same slope, even though the lateral intervals between the extreme curves of a given family may be such as to reduce the later values of the current at a given voltage to a minute fraction of the initial values.

Each curve shown, except curve 20, represents a single set of readings; none were repeated, but the general direction of the line in each case is confirmed by the parallel curves obtained at other cathode temperatures. Between point 12 and curve 13 the tube was sealed off and the cathode raised to 2000° K. The conditions for curve 13 were unsteady; this curve is included to show the extent of the reverse displacement between curves 13 and 14. The cathode was kept at 2300° K. for two hours between curves 14 and 15 and for a further twenty minutes between curves 19 and 20. Curve 20 was not taken under good conditions, but since the middle pair of points repeated well this curve may be taken to represent a new state of the cathode.

Figure 7 shows a similar history given by a tube having for cathode a single point of wire ·002 cm. diameter, which had had been slightly etched by oxidation in fused sodium nitrite in order to remove sharp corners. In this case during the exhaustion the anode was heated by the discharge current itself, and the changes, where not shown as

spontaneous, followed on the passage of heavy currents of from two to five milliampres for this purpose. As in the

Fig. 7.



Cathode a single point of ·002 cm. wire, rounded by etching in $NaNO_2$.

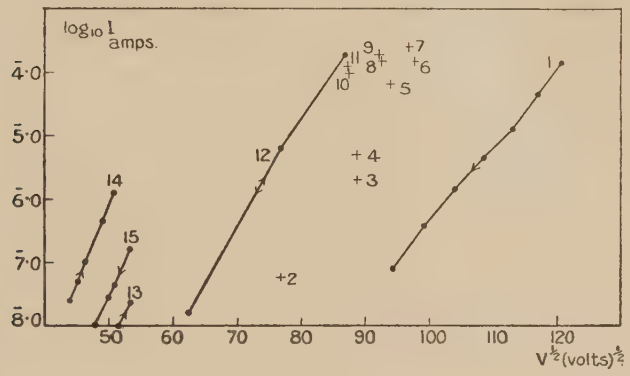
case previously described we have a family of roughly parallel curves, showing successive displacements in the direction of the higher voltages.

(7) *Sodium as a Disturbing Factor.*

Displacements in the direction representing an increase in the current at a given voltage do, however, occasionally occur. Changes of this last sort occurring in valves were known to be associated with the possibility of saline deposits due to attempts to clean the electrodes before bombardment, and it was found that in tubes of the types now under consideration a general tendency for the current to increase, instead of diminishing as in the previous case, could be produced by coating the anode with sodium phosphate. The coating was produced by evaporating a drop of saturated solution. On the first passage of the discharge current, or similarly in the early stages of a thermionic bombardment, the surface of the salt nearest the cathode became black. Then when the anode became hot, and only while the anode was hot, the whole cathode system was outlined by a layer of sodium glow. The current increased by several milliamperes and parts of the cathode system became red hot. These effects were clearly due to the bombardment of the cathode by sodium ions liberated from the anode, as in Aston's positive ray technique for sodium and similar substances. This positive current was well observed in one case where the cathode filament was not fine enough to give the autelectronic discharge, and it was clear that the positive ions were only emitted when the anode, which was heated

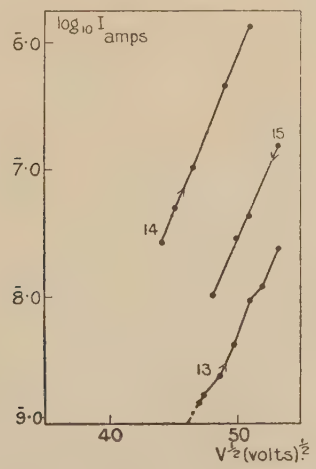
in this case by an auxiliary thermionic bombardment, was at least at a bright red heat. Further evidence of the decomposition of the salt is afforded by the appearance of a green-brown colouration of the nickel anode. The process appears to be a kind of electrolysis *in vacuo*, and it is

Fig. 8 *a*.



1 to 12 voltage from transformer peak; 13 to 15 from D.C. generator.

Fig. 8 *b*.



Cathode a brush of ·002 cm. wires; anode coated with sodium phosphate.

probable that some action of the same kind will always occur when a layer of salt or even the glass itself, particularly in the neighbourhood of a seal, is subjected to electron bombardment.

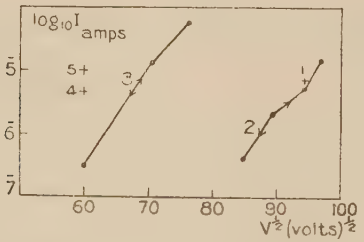
Figures 8 *a* and 8 *b* show the extent of the displacement of

the curves in a tube in which sodium phosphate had been decomposed in this way. The sodium glow was only visible at first. Figure 8 *b* is on a larger scale; a direct-current dynamo was used as the source of high potential in this case.

The first observations, curve 1, fig. 8 *a*, were taken after the tube had been sealed off from the pump, points 2 to 11 after passing heavy currents of a milliampere or more with the sodium glow on the cathode at first, curve 12 after moderate currents of ·2 to ·5 m.a. without glow. There was an interval of nearly four years between the taking of curve 12 and curve 13. The effect of introducing sodium into the tube is thus in great measure permanent, although it could be still further enhanced by the passage of currents of suitable strength as shown by the later curves.

Figure 9 shows a similar case for a cylindrical cathode used

Fig. 9



Cathode a loop of ·0016 cm. wire; anode coated with sodium phosphate.

with an anode coated with sodium phosphate. The cathode being cylindrical, not pointed, the final point 5, 3600 V., indicates a very appreciable current for what is in these experiments a very weak surface field.

The effect of sealing off—unless great care is taken to prevent accumulation of the evolved gases—is always to annul in part the effect of the sodium. A similar effect can be produced by heating the whole bulb to 400° C. while still connected to the pump.

The general tendency where sodium is present in excess is for the curves to be displaced with little or no change of slope in the direction of higher current or lower voltage. It is natural, therefore, to conclude that the sodium is in some way responsible for such displacements, and conversely that the displacement in the reverse direction, illustrated in the cases first described, represents the gradual elimination of traces of sodium or similar substances.

In the case illustrated by fig. 7, a residue of the sodium nitrite used in etching the cathode may have been present initially.

A more general origin of these substances may be the volatilization of alkali compounds from the glass when it is heated to 400° C. in the early stages of the exhaust. This would account for the universal occurrence of these initial displacements, the transitory nature of which so badly masks the main autelectronic effect. Again, O. W. Richardson * has shown that potassium ions are invariably emitted from a positively charged surface composed of any metal when first heated in a vacuum, and that this potassium emission is sometimes followed by a similar sodium emission.

The displacement in the direction of the higher voltages agrees with Millikan's † account of the progressive rise in the voltage required to produce a spark discharge between metal electrodes placed a few millimetres apart in a good vacuum; it seems probable that sodium or a similar substance may be the "impurity" discussed by him in his later paper.

(8) *Temperature effects.*

We may now turn to a more detailed investigation of the effect of the cathode temperature on the autelectronic discharge. The loop filament cathodes used were suitable for observation of the thermionic and autelectronic effects side by side, and throughout these experiments, whenever the temperature was high enough for the thermionic currents to be measurable, these were found to conform to Schottky's relation‡ for the effect of a strong field on a thermionic emission.

The effect of the temperature on the autelectronic discharge was, however, totally different and far more complex. In the first place there is not necessarily any effect at all. In a large number of cases the temperature, as inferred from the heating current passed through the filament, could be raised throughout the range from 300° K. to 1600° K. without appreciable effect on discharge currents of the order of 10^{-4} ampere. Where higher currents of the order 5×10^{-5} ampere were observed the effects, if any, were so small as to be masked by spontaneous variations. Lilienfeld mentions a similar absence of effect on the

* Proc. Roy. Soc. A, lxxxix. p. 507 (1914); also 'Emission of Electricity from Hot Bodies,' p. 218, Ch. VI. 2nd ed. 1921.

† *Loc. cit.*

‡ *Phys. Zeit.* xv. p. 872 (1914).

discharge current when the temperature is lowered to 80° K. by means of liquid air.

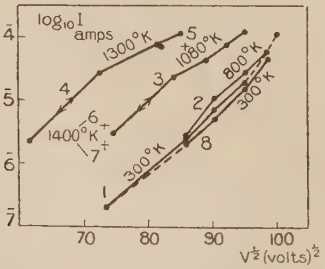
The conditions for this independence of temperature seem to be that the discharge shall be steady, and in particular free from tendency to spontaneous variation in the direction of decreasing current. A tendency to slow, continuous increase of current with the cathode at 1600° K. is a sure indication that subsequent lowering of the temperature will have no effect.

Two cases are particularly remarkable. In both of these a current of 10^{-5} ampere was obtained at 3600 volts, an unusually low voltage for a cylindrical cathode. The one tube (see fig. 9) had been provided with an excess of sodium, and in the other the observations in question were made immediately after the high-frequency heating stage of the exhaust, a condition favourable to at least a temporary sodium effect. Since in both of these cases temperatures up to 1600° K. had no effect, it must be concluded that the sodium effect persists even at such high temperatures, as Langmuir and Kingdon * have found for thermionic emission from caesium up to 900° K. In both cases, however, a subsequent rise to 2080° K. destroyed the sodium effect in part, and necessitated an increase of the voltage to 7000 V.

The temperature effect, when it does exist, is thus a secondary phenomenon characteristic of the stages of transition in the direction of the higher voltages, such as we have ascribed to the progressive elimination of sodium or similar substances †. This view is supported by a closer examination of such regularities as have been observed.

Figures 10 *a* and 10 *b* show the effect as observed at an

Fig. 10 *a*.



On first heating.

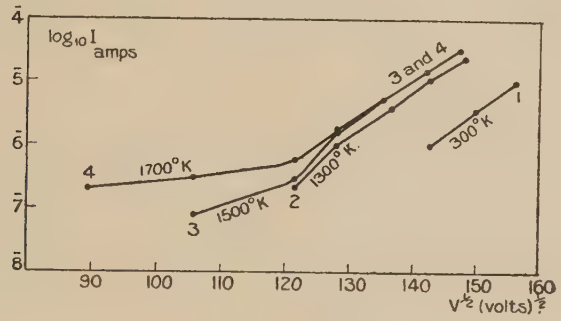
* Phys. Rev. xxi. p. 380 (1923).

† Compare R. C. Burt's observations, Phil. Mag. xlix. p. 1168 (1925), in the similar effect on photoelectric currents of impurities condensible on liquid air.

early and at a late stage in the transition for a particular cathode. The room temperature curves of fig. 10 *a* are the same as curves 10, 11 of fig. 6, and that of fig. 10 *b* as curve 16 of fig. 6.

In both cases the temperature change was reversible, in fig. 10 *b* very strictly so. Compared with the variation of thermionic emission with temperature the effect is, however, very small. Here we double or treble the absolute temperature, and yet the result is no more than would be produced by a change of a few per cent. in temperature in the thermionic case. The effect of a given rise of temperature is to increase all currents in about the same proportion.

Fig. 10 *b*.



After heating to 2300° K.
Cathode a loop of ·0016 cm. wire.

This on the diagram means a simple displacement of the current voltage curve, with little or no change in slope. This is in marked distinction from the thermionic case, where according to Schottky's law the slope should be inversely as the temperature. The mode of variation of the current with the temperature is not at all simple. As the temperature is progressively increased the effect on the discharge-current is small at first, larger later, and then progressively smaller again. Actually there is an optimum temperature for any given state of the cathode, and if this is exceeded the effect becomes more complicated ; higher temperatures produce displacement in the direction of higher voltage, *e.g.* fig. 10 *a*, and the effect is no longer reversible, the room temperature curve being displaced in the same direction. When the temperature is changed there are frequently signs of a small time-lag, illustrated by the first points of curves 2 and 3 (fig. 10 *b*).

With regard to the transition from the thermionic to the autelectronic effect shown in fig. 10 *b*, it must be emphasised that this transition is merely apparent. The curves shown cannot be taken as evidence of physical transition. On the contrary, in each of the four discharge-tubes under observation, while the thermionic bombardment was uniform, the autelectronic discharge was observed to be accompanied by the usual local luminescence or heating of the anode. That the source of the discharge was situated on the filament and not on any other part of the cathode system was made clear by the elongation of the luminescent patches whenever, as sometimes happened, the filament loop went into a sustained vibration of one or two millimetres amplitude tranverse to the plane of the loop. What curve 4 (fig. 10 *b*) shows is therefore the addition of an autelectronic current emitted by a small area to a thermionic current of similar total value, but emitted from a far larger area. The autelectronic current increases so rapidly with the field that it very soon masks the thermionic current in the diagram as plotted. All that the two effects have in common is the tendency of the logarithm of the current to vary as a low power of the voltage, which in those cases where the voltage variation covers a sufficient range can be approximately located as the square-root. The coefficient of variation as indicated by the gradients of the current-voltage curves is quite different for the two effects.

(9) *Observations on Larger Currents.*

In the foregoing detailed consideration of the experimental conditions influencing the discharge, we have confined our attention to currents of 10^{-4} ampere and less. In the majority of the experiments quoted, current readings up to one or two milliamperes were, however, taken, and up to this point continuous curves could usually be obtained. If, therefore, the low-current part of the characteristic was displaced in any particular way, the high current part was similarly displaced. The chief qualitative difference between the two ranges was the greater tendency to spontaneous displacement when the higher currents were passing. If the discharge circuit included a series resistance, and still better if the filaments of the rectifier valves were dulled so as to approach saturation, the extent of the displacement was limited, and currents of the order of 2 milliamperes mean value could be passed for several hours without variation of more than about 20 per cent. When the conditions were such that low voltages, under 7000 V., could be used,

currents of 5 m.a. mean value could be observed, but at higher voltages or with higher currents, the melting of the nickel anode under the intense local bombardment characteristic of the autelectronic discharge made continuous observation impossible.

In one case where a tungsten anode was used momentary currents of much higher value, about 100 m.a., were obtained.

As regards the form of the current/voltage relation for these higher currents the general conclusion, when due allowance has been made for the effect of pulsation of the applied voltage, is that there are no grounds for supposing that for discharge currents of peak value as great as 30 milliamperes the form of the relation differs in any marked way from that more definitely established for smaller currents of one-tenth of a milliampere or less.

(10) *The Current Density at the Emitting Surface.*

None of the experiments described in this paper give any precise information as to the extent of the emitting area from which the discharge pencil emerges from the body of the cathode. Some observations have, however, been made which enable us to set an upper limit to the emitting area, and therefore a lower limit to the current density at the cathode surface. With a cathode consisting of a fine tapered point of final diameter ·0002 cm. a peak current of 30 milliamperes has been obtained. In such a case the emitting area is most probably part of the end of the point. If this is taken to be a hemisphere of diameter ·0002 cm. its area will be $1{\cdot}2 \times 10^{-7}$ cm^2. Now it occasionally happens that a number of discharge pencils can be seen to be existing simultaneously. In the case of these very fine points as many as four have been seen. The area allotted to a single pencil need not therefore be greater than 3×10^{-8} cm^2. A current of 3×10^{-2} ampere uniformly distributed over this area corresponds to a current density of 10^6 amperes per square cm. This likelihood of a high current density provides an explanation for the brilliant white scintillations on the cathode surface, such as are frequently observed when it is first used. It is not uncommon, particularly if the series resistance in circuit is insufficient, for the scintillations to appear to be extended like the track of a meteor as a bright line, straight or curved, which may on reaching the wall of the bulb return at an angle such as would correspond to the rebound of a flying particle. If we suppose that there are adhering to the cathode surface flakes

of conducting material which are not in good thermal contact with the body of the cathode, the passage of the discharge might easily raise these flakes to incandescence, and even melt them. In this latter case the mechanical force on the cathode surface due to the electric field would tear away the molten particle and project it across the space. Millikan's "hot spark" may represent the form taken by the same effect when the discharge is very powerful.

On this view the scintillations are a secondary effect dependent on a peculiar type of local irregularity of the cathode surface.

A similar though milder local heating must occur in the case of the fine point we have just been considering. Here the root-mean-square of the pulsating current of peak value 30 milliamperes was found to be about 12 milliamperes R.M.S. Now a current of 12 m.a. passed through a long wire of the full diameter ·002 cm. would raise its temperature to about 900° K., and would easily fuse a long wire of the diameter, about ·0002 cm., of the end of the point. The temperature actually attained by the point must therefore have been high, unless some limiting agency was present. This may have been the thermal conduction back to the full diameter wire. More probably also the surface cooling effect, which is very important, and perhaps all-important at high current densities, may have kept the temperature down. However, there may have been some temperature rise, for in this, as in many other cases, the effect of passing the heavy current was to displace the characteristic in the same way as those of the loop cathodes when these were raised to a general temperature of 1500° K. or so.

(11) *The Order of Magnitude of the Surface Field.*

We have seen that the autelectronic current increases continuously with the applied voltage, and that there is no evidence of a critical value of the voltage at which the discharge suddenly appears. Since, however, we know little about the current density at the cathode in any particular case, we must for the present select arbitrarily a value of the total current at which to compare cases ; and since the current varies rapidly with the voltage we can, without any risk of confusion, take any convenient value of the current for this purpose. On grounds of the number of observations available a standard current of 10^{-6} ampere

is most convenient. As we have just seen, it is probable that the current density corresponding to this current is far greater than that usual in the study of thermionic emission.

In the case of the loop cathodes made of drawn tungsten wire of diameter ·0016 cm., the extreme values of the voltage for which a current of 10^{-6} ampere has been obtained are about 3000 and 25,000 volts ($V^{\frac{2}{3}}$ 55 to 160).

The field at the surface of a smooth fine cylinder of radius and at voltage V above its surroundings, assumed remote, being $\dfrac{V}{r \log_e \frac{1}{r}}$, and the value of $r \log_e \frac{1}{r}$ for r equal to 8×10^{-4} cm. being $5{\cdot}7 \times 10^{-3}$, the fields corresponding to the voltages given will be $5{\cdot}3 \times 10^5$ and $4{\cdot}4 \times 10^6$ volts per centimetre.

Since, however, any local irregularity of the surface will result in a local increase of field these numbers must be regarded as minimum estimates. Since again the discharge is observed, in the case of cylindrical cathodes very clearly, not to be uniform over the surface, but on the contrary extremely local, it is very probable that we are concerned with local irregularities of the surface, and therefore higher actual values of the field.

We know also that the lower observed value is associated with the presence of sodium in the discharge tube, but there is some doubt whether the last traces of sodium or similar substances were ever so completely eliminated that we can take the higher value as corresponding to a clean tungsten surface.

It should be remarked, that the mean values of the external field necessary to overcome completely the attraction of the surface, as predicted by Schottky * from his two methods of calculation, are 9×10^7 volts per cm. for a surface of sodium and $2{\cdot}8 \times 10^8$ for a surface of tungsten, with respective factors of uncertainty of $\frac{1}{2}$ to 2 and $\frac{1}{3}$ to 3. Our values are thus respectively 170 and 57 times smaller. We should expect them to be somewhat smaller because they clearly refer to a case where only a small proportion of the available electrons are actually emitted. The observations on pointed cathodes of various apparent end curvatures indicate as far as can be estimated both a similar range of field and similar extreme values.

* *Loc. cit.* p 83.

(12) *The Slope of the Characteristic and the Geometry of the Cathode.*

The slope of the current/voltage characteristic as plotted, that is, the value of the gradient $p = \frac{d \log_e I}{d V^{\frac{1}{2}}}$ is not always the same for a particular cathode, as will be seen in fig. 6; nevertheless, a particular value of the slope may be frequently repeated in a family of curves. The tendency to variation in this respect is greatest in the case of the cylindrical cathodes, perhaps because the much greater area exposed to the strong field provides a greater choice of possible local discharge points. Even with a cylindrical cathode, however, the least value of the gradient, *e. g.* curves 13 and 20 (fig. 6), is as much as $\frac{1}{3}$ of the greatest, while the greatest gradient is the most common. There is some slight evidence of the existence of definite alternative slopes. If this is true it may perhaps be the result of the crystalline orientation of the local eminences from which the discharge springs.

In the case of the gradient of the characteristic function, as in that of the field-strength for a given current, the values obtained from the pointed cathodes agree with those from the cylindrical as nearly as estimates of the form of the point will allow.

Taking an unweighted average of all observations we obtain :— $\frac{\log_e I}{df^2} = \cdot 017$, with maximum values about ·026 and minimum about ·009, f being in volts per centimetre.

The corresponding gradient observed for a general thermionic emission from the same cathode wire was ·0013 in the same units, a very much smaller value.

(13) *Theory.*

Since the most definite theory of the autelectronic discharge proposed hitherto is that of Schottky, it is of interest to consider if the results recorded can be interpreted according to it.

Schottky's theory is based on an interaction between the external applied field and the internal field which determines the "work-function," or the energy which an electron has to expend in order to emerge. This internal field is supposed to arise from an attraction between an electron and its electrical image in the surface or images in the surface atoms of the metal.

The external field decreases the effective value of the work-function; if v_0 is the normal work-function in the absence of an external field, and if f is the imposed external field, then v, the effective work-function, is given by

$$v = v_0 - \epsilon^{\frac{1}{2}} f^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e is the electronic charge.

There are good grounds for supposing that Schottky's principle, expressed by (1), must enter into the explanation of any electron emission effect which is influenced by the surface field; for the agreement of the values of the work-function derived from phenomena so different as the thermionic and photoelectric effects indicates that the work-function is a property of the surface in relation to the emitted electron and is not concerned with the actual mechanism of emission.

We shall in the first place consider whether the aut-electronic effect has anything in common with the fact predicted and observed by Schottky * that a thermionic current increases considerably if a sufficiently strong field is applied.

According to Richardson's theory of the thermionic effect the electron current I flowing from the surface at temperature T can be expressed by

$$\mathrm{I} = \mathrm{A}\, \mathrm{T}^{\frac{1}{2}} e^{\frac{-v\epsilon}{k\mathrm{T}}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since we shall be concerned only with rough numerical values, it will be permissible to neglect the variation of $\mathrm{T}^{\frac{1}{2}}$ compared with that of $e^{\frac{-v\epsilon}{k\mathrm{T}}}$ and to write

$$\mathrm{I} = \mathrm{A}' e^{\frac{-v\epsilon}{k\mathrm{T}}}.$$

There are other formulæ for the thermionic effect besides (2) which would give us a similar approximate relation.

Now by (1)
$$\mathrm{I} = \mathrm{A}' e^{\frac{\epsilon^{\frac{1}{2}} f^{\frac{1}{2}} - v_0}{k\mathrm{T}}} . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here if T is constant we have

$$\log_e \mathrm{I} \propto f^{\frac{1}{2}} + \text{constant}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Schottky has confirmed this relation experimentally for thermionic emission in a case where $\epsilon^{\frac{1}{2}} f^{\frac{1}{2}}$ was very much smaller than v_0, and some observations of thermionic

* *Jahrb. d. Radioact. u. El.* xii. p. 200 (1915).

emission made in the course of our experiments are in agreement with his results (*cf.* curve 4, fig. 10 *b*).

Our measurements, so far as the relation (4) is concerned, are consistent with this application of the theory although, as already mentioned, the accuracy is not so great that they can be held to confirm it. They are, however, completely inconsistent with any such variation of the current with the temperature as is given by (3). A simple numerical calculation of actual values of the exponent in (3) shows this at once.

If (4) represents our measurements at all it does so while f varies in the ratio of 2 to 1; the assumption of any smaller variation is still more unfavourable to the possibility of consistency. Let us determine the maximum possible effect of such a variation in f on the exponent. The variation of f will have more effect the larger the ratio of $\epsilon^{\frac{1}{2}}f^{\frac{1}{2}}$ to v_0. Let us suppose then that the upper value of f makes $\epsilon^{\frac{1}{2}}f^{\frac{1}{2}}$ equal to v_0. The lower value of f will now give a value of the numerator of the exponent less than v_0, the value where there is no field, in the ratio $1-(\frac{1}{2})^{\frac{1}{2}}$ to 1, *i. e.*, 0·3 to 1.

The effect of such a change can be seen at once if we suppose it due to an increase in the denominator instead of a decrease in the numerator.

A reduction in the same ratio would have occurred if the temperature T had been increased in the ratio 3·3 to 1, that is, from a room temperature value of 300° K. to 1000° K. Such an increase of temperature would not produce any measurable thermionic emission even from the whole area of the cathode; nor, therefore, should the application of our field.

Further, if we heat the cathode generally to 1500° K. and apply the field the new value of the exponent will correspond to a temperature of 5000° K.

With a change in the exponent corresponding to a change of temperature from 1000° K. to 5000° K. the thermionic emission from tungsten would increase 10^{18} times, so therefore should the current emitted under the influence of the field when the cathode is raised from room temperature to 1500° K.

What we have found in our experiments is that measurable currents can be obtained from a small area of the cathode and that there is no certain change consequent on heating from 300° K. to 1500° K. There is thus complete inconsistency between our observations on the autelectronic

current and the relation (3), and therefore with any extension to lower temperatures of Schottky's modification of the theory of thermionic emission.

Since our observed current/voltage relation is of the form (4) it is of course possible to calculate the value in that relation of the coefficient corresponding to kT in (3).

It may perhaps be of speculative interest to do so. Using our observed value of the gradient $\frac{d \log_e I}{d f^{\frac{1}{2}}}$ and a correction factor of 50 for the true value of the field—as we shall shortly explain—our maximum estimate of the value of this coefficient lies between the limits 1·0 and $2{\cdot}8 \times 10^{-12}$ erg, and is most probably about $1{\cdot}5 \times 10^{-12}$ erg.

Expressed in electron volts these quantities become 0·6 to 1·8 volts, probably about 1·0 volt, or, dividing by k, as hypothetical temperatures 4800° K. to 14,000° K. probably about 7500° K.

This, however, is a parenthesis of no immediate utility, since (4) is and remains an empirical relation.

Returning to the main question, if $\epsilon^{\frac{1}{2}} f^{\frac{1}{2}}$ is greater than v_0, the current will on Schottky's theory be independent of the temperature and of the kinetic energy of the electrons in general, for this will then no longer be required in order to make them emerge. Schottky contemplates such a case, and uses it to obtain an estimate of f, as we shall shortly do.

He cites as possible factors limiting the current, the space charge outside the range of the molecular fields and, possibly, the flow of the electrons through the metal to the point of emergence. Neither of these limitations would be expected to cause the current to vary so rapidly with the field as it does in our experiments; but since he does not carry the theory to the point of making any definite prediction of the relation between the current and the field in these circumstances, this objection perhaps should not be stressed. The only test that can be applied now is whether the measured values of the field are consistent with $v<0$ and the known values of v_0.

If f were taken to be the value of the field over the general surface of the cathode, its value would be far too small. But since the discharge is localized in a few isolated spots this assumption is improbable; it is much more probable, as Schottky supposes, that there are sharp points at these spots which increase greatly the local values of f. On this view we have no direct way of estimating the local value of f, but the following indirect method seems permissible.

According to Schottky's theory, the spontaneous variations of the current are due either to variations of f or to variations of v_0. Since the presence of sodium or other electropositive substances seems one of the main factors determining the variations, it is natural to attribute them to changes in v_0. Indeed, we may assume plausibly that the highest and lowest fields required to produce a given current from the same point correspond to the values of v_0 characteristic of tungsten (v_1) and of sodium (v_2). We may further assume—this is less plausible, but the displacement of the curves without change of slope supports it—that the change from a tungsten to a sodium surface is accompanied by no change in the geometrical form of the surface, and by no change of the relation of f to v, the voltage between the electrodes. Let us then compare the fields, f_1, f_2, required to produce the same current for the different values v_1, v_2 of the normal work function. f_1/f_2 is known from the ratio of the measured voltages; and we have

$$\epsilon^{\frac{1}{2}} f_1^{\frac{1}{2}} - v_1 = \epsilon^{\frac{1}{2}} f_2^{\frac{1}{2}} - v_2$$

or

$$f_2 = \frac{(v_1 - v_2)^2}{\epsilon} \left[\left(\frac{f_1}{f_2} \right)^{\frac{1}{2}} - 1 \right]^2 .$$

Values of f_1/f_2 ascribable to change in the normal work-function have been observed as high as 4/1. Taking the value of v_1 for tungsten as 4·5 volts and that of v_2 for sodium as 2·0 volts we obtain for the value of f_2 $1{\cdot}5 \times 10^5$ e.s.u. per cm., *i. e.* $4{\cdot}5 \times 10^7$ volts per cm. Now for any of the forms of cathode we have used the value of f_2 calculated from the applied voltage and the general form of the cathode varies between 4×10^5 and 2×10^6 volts per cm. according to the value of the current.

It appears then that if the conditions do correspond to values of v approximating to 0, the points from which the discharge proceeds must be so sharp that the local field is about 100 times greater than the general field. This conclusion is perhaps not wholly impossible in itself; Schottky* estimates that points may increase the local field 10 times, but there does not appear to us anything in his argument which necessarily sets a limit at this value.

While, therefore, our experiments are not necessarily inconsistent with the basis of Schottky's theory, we do not think that it can be said to derive any additional support

* *Loc. cit.* p. 78. There is, apparently, a repeated misprint of $2k$ for 2^k here.

from them. We have no extension of his theory nor alternative theory to propose, not because none is imaginable, but rather because we cannot find any which can be supported by our experiments. Thus, it is not impossible to deny the assumption made throughout the foregoing argument, that the temperature of the spots from which the discharges proceed is the same as that of the main portion of the cathode ; sharp points may be heated by the discharge itself until they are capable of a normal thermionic emission ; some support for this view might be found in the scintillations that were mentioned in section (10). On the other hand, as we have seen, local emission currents have been observed sufficient to have fused the whole cathode, and yet the sharp point supposed responsible for the emission was little affected and certainly not destroyed.

Again the whole explanation may lie deeper and have to be sought, as Schottky suggests, in terms of space lattices or quantum orbits of the electrons in the metal rather than in terms of a mean kinetic energy. The discussion of these possibilities is, however, best postponed until further facts are available.

LIII. *The Determination of Minima-Maxima Forces in certain Problems of Dynamic Balance. By* P. Field Foster, *B.Sc., University College, Cardiff, and* J. F. Baker, *B.A.**

CERTAIN problems in dynamic balance require the determination of the smallest maximum value of a rotating force vector and the corresponding angle, resulting from the composition of a vector $\alpha = P\left(\cos\theta + \frac{1}{n}\cos 2\theta\right)$ with a vector $\beta = -W$, where β revolves with uniform angular velocity and α oscillates along a fixed direction OQ, and is a function of the angle θ made by β with the same direction, both vectors having the same origin.

The vector diagram, fig. 1 (*b*), indicates clearly the nature of the forces. It is to be observed that the angle θ is measured from the positive direction of the oscillating vector.

In the expression $P\left(\cos\theta + \frac{1}{n}\cos 2\theta\right)$, P and n are

* Communicated by Dr. W. T. David, M.Inst.C.E.

constants. The resulting force F is given by

$$F^2 = P^2\left(\cos\theta + \frac{1}{n}\cos 2\theta\right)^2 - 2PW\left(\cos\theta + \frac{1}{n}\cos 2\theta\right)\cos\theta + W^2. \quad . \quad . \quad (1)$$

For simplification let $W = kP$ and $P =$ unity, so that $W = k$,

then $$F^2 = \left(\cos\theta + \frac{1}{n}\cos 2\theta\right)^2 - 2k\cos\theta\left(\cos\theta + \frac{1}{n}\cos 2\theta\right) + k^2. \quad . \quad . \quad . \quad (2)$$

Given k, F can be found for any angle θ.

The particular value required in this instance is not forthcoming by treating F as a function both of θ and the parameter k, obtaining maximum values and then solving for a minimum, or *vice versa*, by the usual methods.

Some idea of the change in the cyclical variation of F with the parameter k can be obtained from an inspection of the diagrams in fig. 1. It will be seen that as k increases

Fig. 1 (*a*).

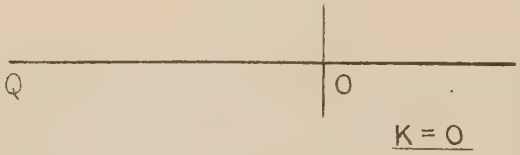
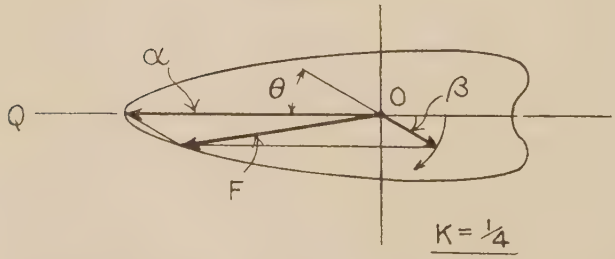


Fig. 1 (*b*).



from zero, fig. 1 (*a*), the maximum value of the radius vector F_{max}, which at first is along the initial direction, viz. $\theta = 0$, becomes reduced in magnitude until, when a particular value of k is reached, three equal values of F_{max} arise, one lying along the fixed direction whilst the other two are equally inclined to the same direction, but are on opposite sides of it, fig. 1 (*d*). Further increase of the parameter leads to two equal values of F_{max}, as can be seen from an inspection of the remaining figures.

Fig. 1 (*c*).

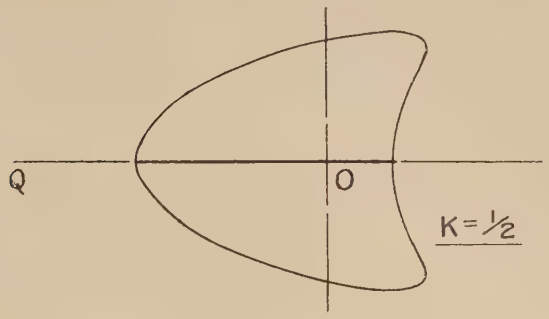


Fig. 1 (*d*).

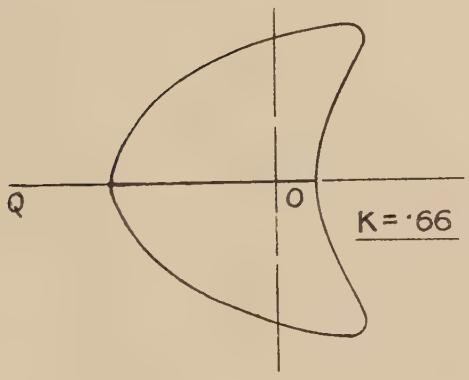
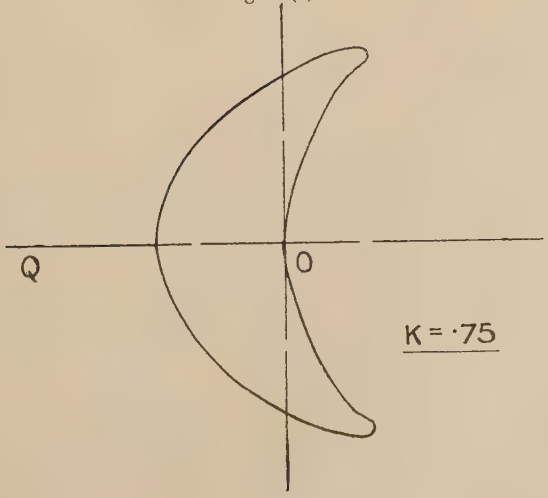
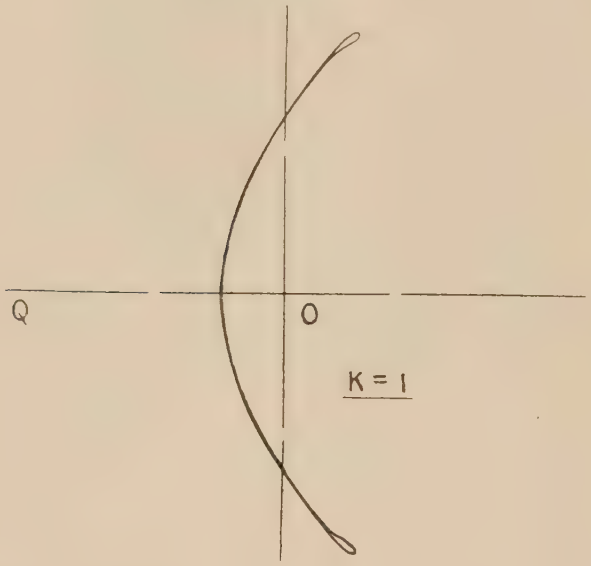


Fig. 1 (*e*).



In this, and similar cases, where a minimum-maximum is sought, and which cannot be evaluated by the usual methods, it is necessary to consider each case *per se* and to obtain the solution, should one exist, by particular methods. The case under consideration can be solved in the following manner, n being known.

Fig. 1 (f).



We have, taking $n=4$,

$$F^2=\left(\cos\theta+\frac{1}{4}\cos 2\theta\right)^2-2k\cos\theta\left(\cos\theta+\frac{1}{4}\cos 2\theta\right)+k^2.$$

For $\theta=0$, $F=\left(\frac{5}{4}-k\right)$, taking the positive root. In the case when k is such that a minimum-maximum value of F results, the value of F for $\theta=\theta_1$ (say) is the same as for $\theta=0$.

Let $x=\cos\theta$, then when the value F_{θ_1} is equal to the value F_{θ_0} we must have

$$\left(\frac{5}{4}-k\right)^2=\left\{x+\frac{1}{4}\left(2x^2-1\right)\right\}^2-2kx\left\{x+\frac{1}{4}\left(2x^2-1\right)\right\}+k^2,$$

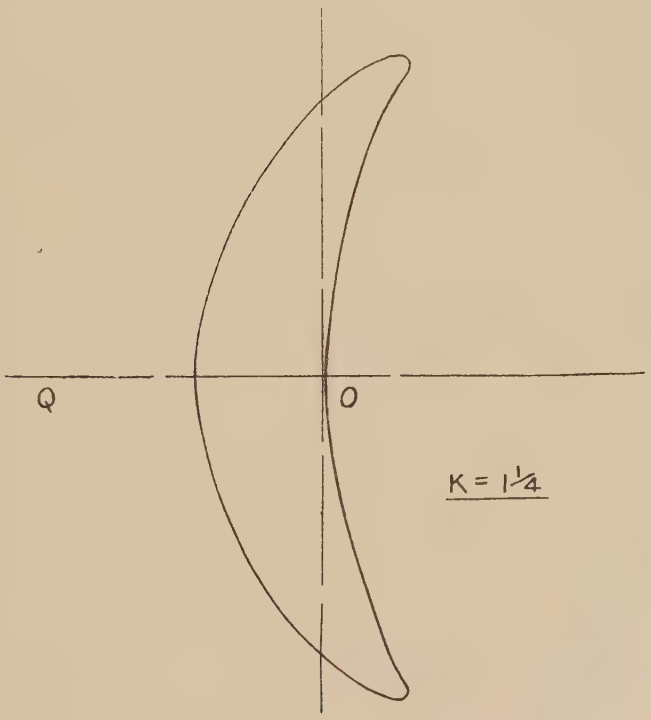
which after reduction becomes

$$\frac{3}{2}-\frac{5}{2}k=\frac{x^4}{4}+x^3\left(1-k\right)+x^2\left(\frac{3}{4}-2k\right)+x\left(\frac{k}{2}-\frac{1}{2}\right). \quad . \quad (A)$$

We thus have one relation between $\cos\theta$ and k.

If for a given value of k we consider the graph connecting F with θ, at maxima and minima values, if any, we shall have $\frac{\partial F}{\partial \theta} = 0$, and hence another relation between cos θ and k.

Fig. 1 (*g*).



Differentiating then, equation (2) with regard to θ, equating to zero and replacing cos θ by x, we have

$$2x^3 + 6x^2(1-k) + x(3-8k) + k - 1 = 0. \quad . \quad . \quad \text{(B)}$$

The equations (A) and (B) can be expressed as

$$\text{(A)} \equiv x^4 + bx^3 + cx^2 + dx + e.$$

$$\text{(B)} \equiv x^3 + fx^2 + gx + h.$$

Eliminating x we have

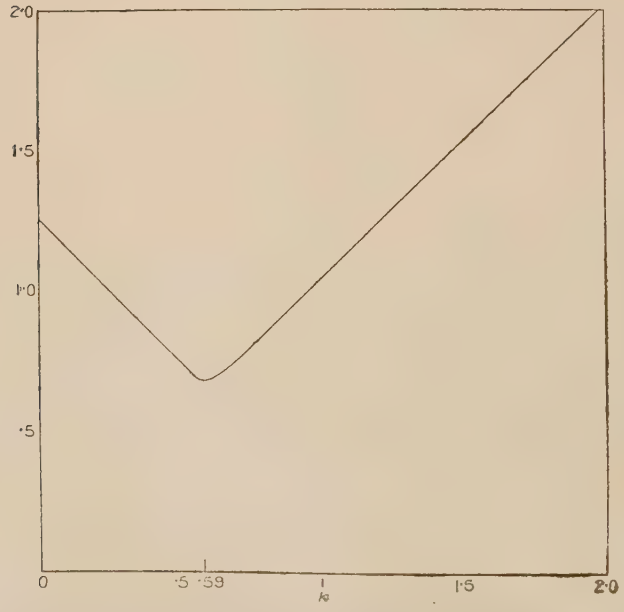
$$\begin{vmatrix} 0 & 0 & 1 & b & c & d & e \\ 0 & 1 & b & c & d & e & 0 \\ 1 & b & c & d & e & 0 & 0 \\ 0 & 0 & 0 & 1 & f & g & h \\ 0 & 0 & 1 & f & g & h & 0 \\ 0 & 1 & f & g & h & 0 & 0 \\ 1 & f & g & h & 0 & 0 & 0 \end{vmatrix} = 0.$$

Expanding the determinant and substituting for b, c, d, etc. their values in terms of k we have finally

$$676k^6 - 2561k^5 + 3299\frac{13}{16}k^4 - 2089\frac{1}{4}k^3 + 1072\frac{1}{16}k^2 - 557\frac{1}{4}k + 139\frac{3}{8} = 0, \quad . \quad (3)$$

from which $k = \cdot 588$ very closely. This is the smallest positive root, and the only one lying between zero and

Fig. 2.



unity ; hence this value of k is the one required. The equation for k may be written with the coefficients expressed

in terms of n, but in view of their complicated forms it has been thought advisable to illustrate the method by means of a numerical example.

By plotting the maxima values of the unbalanced force as determined from the diagrams of fig. 1 (together with additional values found in like manner), the curve shown in fig. 2 is obtained. This curve is almost a Vee and careful plotting is necessary in order to determine accurately the shape of the curve in the region of the vertex. The value of k determined in this manner is 0·59, which agrees closely with the value found from equation (3). The corresponding value of θ is easily determined.

The authors hope to publish some further results in this connexion at a future date.

LIV. *An Experimental Verification of Gibbs' Adsorption Equation by observing the Adsorption by Mercury of its own Ions from Solution, and its bearing on Nernst's Theory of Electrode Potential.* *By* R. KENWORTHY SCHOFIELD, *B.A., Trinity College, Cambridge* *.

§ 1. *Historical.*

WARBURG [1] showed that the surface-tension of the interface between mercury and a solution of mercurous nitrate in nitric acid varies with the concentration of the mercurous salt, and concluded that the salt is adsorbed at the interface in accordance with Gibbs' adsorption equation. He sought to explain the change in surface-tension of the cathode of a capillary electrometer as the result of a change in the mercurous salt-content of the neighbouring solution due to concentration polarization. This view gained little headway against the ideas of Lippmann and Helmholtz owing to the rapidity with which the mercurous salt concentration at the cathode decreases with increasing polarizing E.M.F. Gouy [2] considered that a change in the mercurous salt-content of the solution affects the surface-tension, because it alters the electrical potential difference at the interface and, hence, the repulsive forces in the electric boundary-layer, rather than because the mercurous salts exert "capillary" forces at the interface.

Lewis [3], and later Patrick [4], found that mercurous sulphate is removed from aqueous solution in the neighbour-

* Communicated by Dr. E. K. Rideal.

hood of a nozzle delivering a stream of mercury drops. They concluded that the salt is adsorbed on the surface of the drops. Neither succeeded in obtaining a quantitative measure of the amount adsorbed per unit area. Lewis considered that Gibbs' adsorption equation in its original form is not applicable to such a system, and that it is necessary to consider "electrocapillary" adsorption of the mercurous and sulphate ions in addition to "pure" adsorption of the undissociated molecules.

Euler and Hedelius[5], more recently, have observed the decrease in concentration of an aqueous silver nitrate solution on the addition of silver foil. They favour the view of Langmuir that adsorption is due to residual valency forces operating at definitely localized places on the surface, and consider that the success of Nernst's theory of electrode potential demonstrates the chemical attraction of a metal for its own ions. They do not believe capillarity plays any part in the phenomenon, and undoubtedly there are difficulties in dealing with the surface-tension of a solid. With mercury this difficulty is removed, and Euler and Zimmerlund[6], using a method similar to that of Lewis with the addition that its poisoning action on an enzyme was used to measure the mercurous salt concentration, have made a quantitative estimation of the adsorption of mercurous chloride by mercury, and find the amount is sufficient to quarter-saturate a unimolecular layer. No surface-tension measurements were made by which the validity of Gibbs' original equation or Lewis's modification of it might have been tested.

Gibbs[7] and Warburg (*loc. cit.*[1]) gave thermodynamic treatments of the equilibrium of an interface between mercury and dilute sulphuric acid. In this system there exists the equilibrium $2\,Hg + H_2SO_4 = Hg_2SO_4 + H_2$; consequently the thermodynamic potentials of only three of these substances are independently variable. Gibbs regarded the potential of Hg_2SO_4 as dependent on the rest, while Warburg so regarded the potential of H_2; consequently their conclusions, though both thermodynamically correct, differ in form. The thermodynamic potentials of the ions Hg_2'', SO_4'', H', OH', and electrons may all be regarded as independently variable subject to the restriction that there can be no volume charge. The ambiguity of the former treatment disappears, but care has to be taken in relating the potentials to composition and electrical potential of the phases. Van Laar[8] and Frumkin[9] have attempted to

use these variables, but the author does not consider either treatment completely satisfactory.

Nernst[10] attempted to relate his theory of electrode potential to electrocapillarity, but failed to effect a satisfactory union owing to the erroneous idea, current during the closing years of last century, that a mercury electrode showing its maximum surface-tension is necessarily at the same electrical potential as the electrolyte with which it is in contact. This notion has been proved incorrect by the work by Gouy[11], Smith[12], and others, but no attempt has been made to remodel Nernst's theory in the light of this fact.

In § 2 of the present paper an attempt is made to give as concisely as possible the result of applying the thermodynamic methods of Gibbs, and the principles of electrostatics to the equilibrium of an interface between a metal and an electrolyte containing its ions. Part of it is original, but where possible use is made of those parts of existing treatments which appear correct. In this way Nernst's theory, in a form which does not involve the physical existence of an "ionic solution pressure," or the fallacy referred to above, Helmholtz' original theory of the electric *boundary* layer (as distinct from the subsequent particular theory of the *double* layer), Lippmann's equation, and Gibbs' adsorption equation are all inter-related. In § 3 experiments designed to test a conclusion arrived at in § 2 are described. The results besides confirming this are seen in § 4 to support Warburg's original idea, and the views of Gouy, of Lewis, and of Euler and Hedelius are there discussed.

§ 2. *Theoretical.*

According to Gibbs[1] any constituent of a system in equilibrium must have the same thermodynamic potential in all the phases of which it is a component. Hence when equilibrium has been established across an interface between a metal and an electrolyte containing its ions, the thermodynamic potential $\mu_{\text{Me ions}}$ of the metallic ions must be the same in both. In general the thermodynamic potential of a constituent which is electrically neutral may be said to depend only on its concentration C and its "environment," but if it is an ion, the electrical potential of the phase must also be considered. In the present system, if the electrical potential of the electrolyte be reckoned as zero and that of the metal Δ (in volts), the thermodynamic potential of the

metallic ions in ergs per gr. ion will be

$$\left.\begin{aligned}\mu_{\text{Me ions}} &= \mathrm{RT}\log_e \mathrm{C} + k_e \text{ for the electrolyte} \\ &= 96{\cdot}5\times 10^{10} n\Delta + k_m \text{ for the metal}\end{aligned}\right\}, \quad . \quad \text{(i.)}$$

where k_e represents the "environment" in the electrolyte, and is only independent of C when the latter is small, $96{\cdot}5\times 10^{10}n$ is the charge on a gr. ion in coulombs $\times 10^{-7}$, n is the valency of the metallic ions, and k_m embraces both the concentration and "environment" in the metal and is evidently independent of Δ. Hence

$$\Delta = \frac{1}{96{\cdot}5\times 10^{10} n}\left\{\mathrm{RT}\log_e \mathrm{C} - (k_m - k_e)\right\} \quad . \quad \text{(ii.)}$$

In this relation $k_m - k_e$ is proportional to the logarithm of Nernst's "ionic solution pressure" [14], but is seen to depend on the properties of the electrolyte as well as on those of the metal *.

Were it supposed that at an interface the density of each component changed abruptly at an imaginary geometrical surface, being constant on either side into the interior of each phase, the amount of each component actually present in the system would differ from that calculated on this basis by an amount depending on the position chosen for this dividing surface [15]. By a suitable choice, however, the surface excess of any one component can be made to vanish, and in the present system it is convenient to so choose it that there is no surface excess or deficit of metallic ions at the interface, since these are the one constituent present in both phases. In accordance with this convention all the metallic ions in the system are assigned to one or other of the bulk phases.

If at the instant when the metal comes into contact with the electrolyte it is not at the electrical potential necessary for equilibrium, the thermodynamic potential of the metallic ions in the two phases will differ, and consequently some of them will pass from the phase in which their potential is higher to that in which it is lower. This phenomenon may conveniently be called the "Nernst ionic transfer."

* Butler (Trans. Faraday Soc. xix. p. 729 (1924)), and Heyrovsky (Proc. Roy. Soc. A, cii. p. 627 (1923)), have given expressions relating Δ to the molecular properties of the metal and the electrolytes. Their treatments may be regarded as attempts to evaluate k_m and k_e in terms of the ionization potential of the metal and the heat of hydration of the ions in the solvent.

From electrostatic principles Helmholtz[16] derived the expression

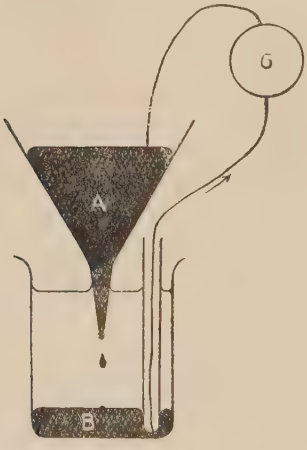
$$\Delta = 4\pi M \times 300, \quad . \quad . \quad . \quad . \quad . \quad \text{(iii.)}$$

where M is the electric moment of the interface in E.S.U. per sq. cm. Hence two phases in contact can only be at a difference of electrical potential Δ when the electrical distribution in the interfacial layer gives rise to the necessary moment. Thus, although the equilibrium value of Δ is determined solely by the chemical composition of the two homogeneous phases, a particular molecular and ionic arrangement must be established in the intervening non-homogeneous layer in order that the conditions of chemical and electrical equilibrium may be simultaneously obeyed. An addition of ions to the metallic phase by means of a "Nernst ionic transfer" will give rise to a surface deficiency of electrons (the other component of the phase); similarly, their removal will cause a surface excess of electrons. Since there can be no net volume charge the surface density of the other ions of the electrolyte with respect to the dividing surface must always have a charge equal and opposite to that of the surface density of electrons. The resulting distribution will give rise to an electric moment the value of which, for bulk phase of given composition, will depend only on the surface density of electrons. The exact relation between these two quantities cannot be deduced from general principles unaided by specific molecular hypotheses. In spite of this it is evident that the "Nernst ionic transfer" will continue until the resulting surface density of electrons is sufficient to set up the moment necessary to give the value of Δ required for the equilibrium of the metallic ions.

If the metal be a liquid, such as mercury, and the interface at which equilibrium has already been established be expanded, a "Nernst ionic transfer" will occur in order to establish at the new surface the necessary surface density of electrons, but it is evidently immaterial whether the transfer occurs at the newly-made surface or on the old. In particular, if the metallic phase be in two parts A and B connected by a wire, and the surface of A be enlarged, equilibrium can be established by a transfer at the surface of B and the passage of an equivalent electric charge along the connecting wire. Moreover, if the surface of A expands at the same rate as that of B is contracting, there will be no change in the total area of the interface, and consequently equilibrium can be maintained simply by a movement of

electrons from one part of the phase to the other, *i.e.*, simply by the passage of a current along the connecting wire, a process by which equilibrium is set up far more rapidly than by the diffusion of ions. Such a system is shown in fig. 1, an arrangement described by Varley[16] and later by Lippmann[17]. If dilute sulphuric acid be the electrolyte, it will attack the mercury if it contains dissolved oxygen.

Fig. 1.



Consequently mercurous sulphate will be present in solution at an appreciable concentration. Under these circumstances the direction of the current which flows through the galvanometer as the drops fall shows that there is a deficit of electrons at the interface at equilibrium *.

Lippmann related the surface electrification, of which these experiments give evidence, to the rate of change of the surface tension σ of the interface (in dynes/cm.) with Δ. His method of deducing this relation has been criticized, but the result is undoubtedly correct, and can be obtained by an application of Gibbs'[18] adsorption equation (at constant temperature)

$$d\sigma = -\Sigma \Gamma d\mu,$$

in which the summation extends over all the *independently variable* components of the system. We may regard these

* An arrangement described by C. T. R. Wilson (Proc. Roy. Soc. A, xcii. p. 505 (1916)) and used by him to measure the passage of charges works on this principle, and depends for its action on the fact that the acid creeps between the mercury and the glass.

as Hg_2'', SO_4'', H', OH', and electrons, since all the constituents present can be regarded as composed of two or more of these. If a change of σ with Δ be considered in which the strength of the sulphuric acid remains unaltered, $d\mu$ for SO_4', H', and OH' is zero, Γ for Hg_2'' is also zero on account of the choice of dividing surface, and only the term relating to the electrons remains. $d\mu$ for the latter is evidently $96{\cdot}5 \times 10^{10}\, d\Delta$. Hence

$$\Gamma_{\text{electrons}} = \frac{1}{96{\cdot}5 \times 10^{10}} \frac{d\sigma}{d\Delta}, \quad . \quad . \quad . \quad \text{(iv.)}$$

$\Gamma_{\text{electrons}}$ being measured in gr. equivalents per sq. cm. If $\Gamma_{\text{electrons}}$ be replaced by its equivalent electric charge, ϵ, in coulombs per sq. cm., we obtain Lippmann's equation

$$\frac{d\sigma}{d\Delta} = \epsilon \times 10^7 . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(v.)}$$

Lippmann measured $d\sigma/d\Delta$ with a "capillary electrometer," a cell of which the cathode is a mercury thread in a capillary tube, so arranged that the surface-tension of the interface can be measured. An E.M.F., V, is applied between this cathode and a mercury anode presenting a large surface to the electrolyte. If the latter is rendered "unpolarizable" by covering it with crystals of the appropriate mercury salt, Δ remains unaltered at the anode and $d\Delta$ at the cathode $= -dV$. Hence $d\sigma/d\Delta = -d\sigma/dV$. The $\sigma - V$, or electrocapillary, curve for sulphuric acid of a strength used by Lippmann is nearly (but as the most recent measurements show, not exactly) parabolic, σ rising to a well-defined maximum value. For other electrolytes, notably KI, the curve is not even approximately parabolic. Guided by Lippmann's measurements on sulphuric acid, Helmholtz [19] attempted to relate ϵ to Δ by means of equation (iii.) by assuming the moment of the interface to be due to a double layer consisting of a charge ϵ on the mercury and a complementary layer of oppositely charged ions at a small distance. The work of Gouy [11], Smith [12], and others has shown that the electrical distribution cannot in general be so simple. In particular Δ is not always zero when ϵ is zero, a fact fatal to the simple Helmholtz theory. The breakdown of the simple double-layer theory does not, however, affect the validity of Lippmann's equation, of which Frumkin [20] has recently obtained experimental confirmation, both by showing that an insulated dropping always takes up the

potential of the maximum of the electrocapillary curve * and also by measuring ϵ quantitatively with an apparatus similar to that of fig. 1, and comparing the values of ϵ thus obtained with those of $d\sigma/dV$ found with a capillary electrometer in the neighbourhood of $V=0$. Frumkin used, besides sulphuric acid, solutions for which the electrocapillary curve is far from parabolic and for which the electric boundary layer is undoubtedly complex. Assuming the general validity of Lippmann's equation $d\Delta/d\epsilon$ is found to be always positive, a condition necessary for the establishment of electrical equilibrium by the "Nernst ionic transfer."

It thus appears that the surface concentration calculated as above with the aid of Gibbs' adsorption equation is equal on the one hand to minus the surface charge found by Lippmann's equation from the slope of the electrocapillary curve and expressed in gr. equivalents per sq. cm., and on the other hand to minus the number of gr. equivalents of mercurous ions taken up by an expanding mercury surface or thrown off a contracting one per unit area in course of the "Nernst ionic transfer."

§ 3. *Experimental.*

In order to test this conclusion experimentally, measurements were made on a modified form of Patrick's "constant flow" adsorption tube (*loc. cit.* [4]). A quantity of dilute sulphuric acid containing mercurous sulphate was rendered oxygen-free by boiling, and stored in a flask in an atmosphere of nitrogen. When cold this solution was driven under nitrogen pressure from an aspirator along a delivery tube and entered the adsorption tube at A (fig. 2).

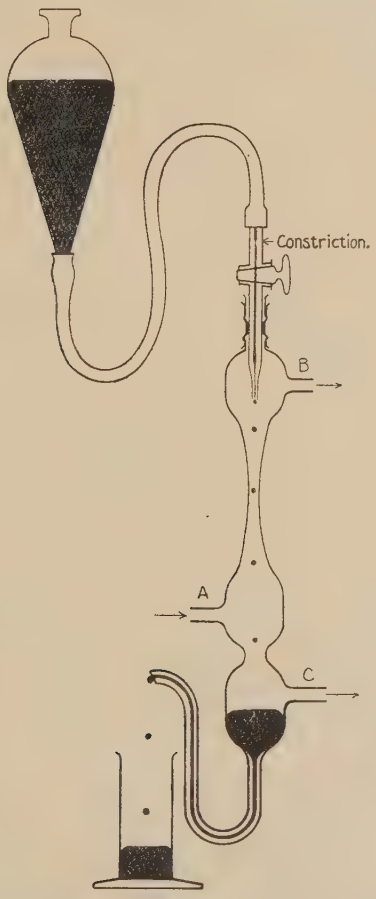
Instead of all passing upwards past the tip from which the mercury drops fell, as in Patrick's experiments, the stream divided, part travelled downwards over the mercury surface into which the drops coalesced at the lower end of the adsorption tube. In this way it was possible to measure the amount of salt adsorbed by the drops in their formation, and also the amount given back to the solution when they disappeared.

The arrangement shown in fig. 3 was used to find the change in concentration of the mercurous ions produced by the falling drops. Preliminary experiments showed that when a stream of the above solution is sent through this apparatus the potential difference between the mercury

* An observation originally due to Paschen (Wied. Ann. xli. p. 42 (1890)); *cf.* also Smith and Moss (Phil. Mag. (6) xv. p. 428 (1908)).

covered with solid Hg_2SO_4 in D and that in contact with the stream in the cup E depends on the speed of the stream as well as on its mercurous salt-content. With the cup E made in a capillary tube, as shown, it was found, however, that this potential difference is constant when the flow-rate

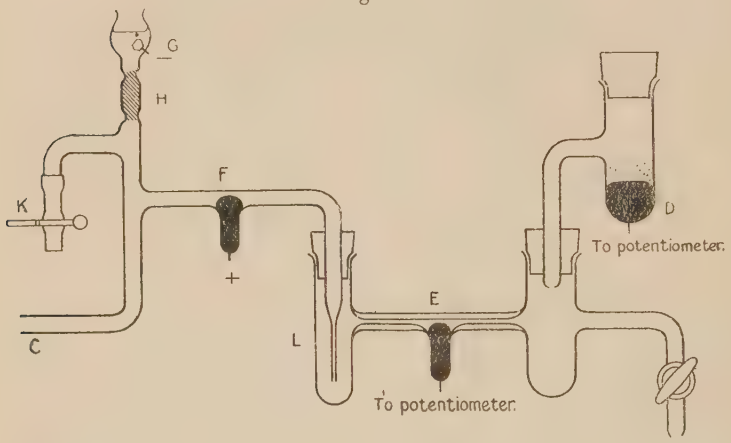
Fig. 2.



exceeds a critical value. The cause of this effect was never satisfactorily traced, but as will be apparent it did not affect the validity of the final results. Mercurous sulphate could be added to the stream before it reached E by passing a current between the mercury cup F (as anode) and the

platinum foil G, from which hydrogen bubbled. The connecting-tube H was filled with 2 per cent. agar-agar jelly, and had two constrictions to prevent the pressure from dislodging it. By means of the side-tube K, the tube joining the agar-tube to the rest of the apparatus could be washed out from time to time, thus preventing any products of the jelly from diffusing into the main stream. In order to overcome the difficulty of mixing the layer of concentrated solution, which was carried away from F uniformly with the rest of the solution, the arrangement shown at L

Fig. 3.



was finally adopted. It was found that with a sufficiently rapid flow-rate the change in the potential difference between D and E was proportional to the current sent between F and G, and inversely proportional to the flow-rate. This was considered a satisfactory indication that the apparatus was reliable.

With the solution leaving the adsorption tube at both B and C (fig. 2) at a rate sufficient for the satisfactory working of "electrolytic injectors" (as the arrangements in fig. 3 may conveniently be called) attached at these points, no mixing occurs between the liquid which flows over the lower mercury surface and that which passes the dropping tip. A quantitative measure of the rate at which mercurous ions are thrown off the drops as they coalesce can therefore be made as follows. A steady flow in at A and out at B and C is set up, and mercury is set dropping from the tip at a uniform rate (siphoning out at the bottom). The solution

entering an electrolytic injector attached at C thus contains the mercurous ions thrown off, the drops in addition to those originally in the solution entering at A. When the potential difference between D and E has become steady it is balanced with a potentiometer, using a sensitive galvanometer. On turning off the mercury drops the solution leaving the adsorption-tube at C is the same as that entering at A, and the potentiometer is consequently thrown out of balance. Without touching the potentiometer the galvanometer can be brought back to zero by passing a current, suitably adjusted by a rheostat, between F and G. It is evident that a measurement of this current enables the number of gr. equivalents of mercurous ions liberated per second by the coalescence of the drops to be calculated, since the rate of liberation of ions by the electrode F must have been exactly equal to this. An "electrolytic injector" attached at B permits of a measurement of the rate at which mercurous ions are removed from the upper stream when the mercury drops are falling, by finding the compensating current necessary to restore a potentiometer balance obtained before the drops were turned on.

Since a minimum flow-rate is necessary for a satisfactory working of the "electrolytic injector," only small changes in the concentration are effected, and it is necessary to have a drop-rate faster than can be counted with the unaided eye if accurate results are to be obtained. The drops were therefore counted with the aid of a rotating stroboscopic disk mounted on a Rayleigh-Wilberforce synchronous motor. The current interrupter used was so constructed that the effective length of the trembler could be varied while the motor was running. In this way the disk could not only be kept rotating at a uniform speed, but also the speed could be altered at will. Using a dropping tube with a constriction in it and a large head of mercury, steady dropping could be obtained up to 30 drops per second, further increase in the head produced a jet. With the aid of a fine adjustment on the height of a reservoir, the drop rate could be kept constant to two per cent. The mercury siphoned steadily out of the bottom of the adsorption-tube without giving rise to any noticeable fluctuations in the level of the mercury. A bell on the synchronous motor rang for every 3000 drops, that is for every hundred turns of the stroboscopic disk which had thirty slits. By weighing the amount of mercury collected between successive rings of the bell, the weight and hence the area of a drop could be found. By finding the time interval between successive

rings the adsorbing area formed at the tip and removed at the bottom per second can be calculated.

Measurements on the stream emerging at C showed that, with solutions of the same composition, the rate of production of mercurous ions is independent of the flow-rate and proportional to the rate of disappearance of drop-surface. The ions simultaneously removed from the other stream by the equally rapid formation of drop-surface at the tip was always less than those given to the lower stream, and the discrepancy was greater the faster the drop-rate and the slower the flow-rate. It become evident that whereas a still mercury surface is not attacked by oxygen-free sulphuric acid, since a drop of mercury placed in the flask containing the solution * caused no measurable increase in the mercurous ion concentration when left undisturbed for several weeks, a rapidly expanding surface is so attacked. It was found that shaking the flask, and thus causing the drop-surface to expand and contract successively, increased the mercurous ion concentration. More shaking always produced more mercurous ions, proving the effect was not due to the formation on standing of a concentrated layer near the still drop, which shaking mixed with the rest of the solution. The action of sulphuric acid on an expanding mercury surface has already been studied by Smith [21], who has in certain cases observed the evolution of hydrogen. The effect was lessened by replacing some of the sulphuric acid by sodium sulphate, but even with a solution $\frac{3}{40}n\mathrm{Na_2SO_4}+\frac{1}{40}n\mathrm{H_2SO_4}$ used in the final measurements there still exists the irreversible production of mercurous ions as the drops are formed. It was not found satisfactory to use a neutral sodium sulphate solution owing to the formation of basic mercurous sulphate, which is not sufficiently soluble.

The final measurements were confined to the lower stream, and the measurements by which the number of gr. equivalents of mercurous ions given to the solution on the disappearance of unit area of drop-surface were calculated are summarized in Table I. for the three strongest solutions used. The measurements necessary are those of a current, a weight and a time in each case. All these can be found to at least one per cent. The reliability of these depend on the accuracy to which the drop-rate was synchronized with the stroboscope and the accuracy to which the potentiometer balance could be observed. The latter was the greater uncertainty as the

* To reduce any mercuric ions that might initially be present.

TABLE I.

E.M.F. in millivolts.	Galvanometer (double) deflexion.	Gr. equivs. liberated per sec. $\times 10^{-10}$.	Time for 3000 drops in secs.	Weight of 3000 drops in grs.	Area of 3000 drops in sq. cms.	Nernst ionic transfer in gr. equivs. per sq. cm. $\times 10^{10}$.	Cc.s. of solution per minute.
18·0	29·0	5·08	125	43·9	152·5	4·16	9·1
,,	28·0	4·82	135	44·4	153·8	4·23	17·5
,,	25·0	4·40	177	52·2	172·2	4·53	11·4
,,	22·5	3·96	180	53·4	173·8	4·09	19·0
						4·23	
30·5	20·2	3·54	198	57·2	182·1	3·85	7·3
,,	19·5	3·41	198	56·9	181·1	3·72	12·9
,,	22·8	3·99	148	49·6	165·5	3·57	12·8
,,	21·5	3·77	174	57·3	182·3	3·61	20·5
						3·69	
42·0	16·0	2·80	188	57·2	182·1	2·89	12·3
,,	21·0	2·32	175	53·5	174·1	3·34	14·7
,,	18·0	3·15	172	55·3	178·0	3·04	18·4
,,	17·3	3·07	184	56·7	181·0	3·12	19·0
,,	16·7	2·86	194	56·1	179·7	3·09	19·5
						3·10	

lack of balance to be corrected by the compensating current amounted to a few millivolts only, and this entirely accounts for the differences between successive observations on the same solution. The E.M.F. in the first column is a measure of the concentration of the solution.

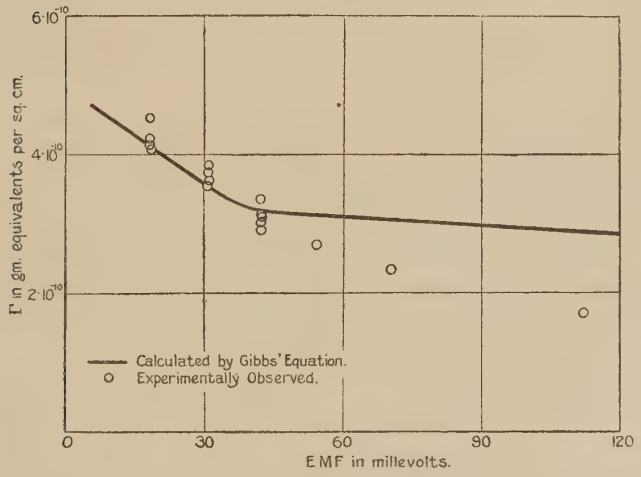
To obtain the values of $\Gamma_{electron}$ given by Gibbs' adsorption equation, a capillary electrometer similar to that used by Smith (*loc. cit.* [12]) was set up. The anodic mercury was covered with mercurous sulphate, and the same solution, $\frac{3}{40}n\mathrm{Na_2SO_4} + \frac{1}{40}n\mathrm{H_2SO_4}$, was used as in the previous experiments. The distance from the capillary meniscus to the top of the column at the maximum of the electrocapillary curve was 25·2 cm. Gouy's [22] value for the maximum surface-tension is 427 dynes/m., hence 1 cm. of mercury corresponded to $427/25{\cdot}2 = 16{\cdot}9$ dynes/cm. The changes in surface-tension between $V=0$ and $V=0{\cdot}12$ were accurately determined by applying air-pressure, recorded on a water-manometer, to the top of the mercury column of which the height was not altered. The applied E.M.F. and water-manometer readings are given in the first and second columns of Table II. over a sufficient range for comparison to be made with Table I. One centimetre of water corresponds to $16{\cdot}9/13{\cdot}56 = 1{\cdot}25$ dynes/cm. The change of surface-tension between 10 and 20 millivolts is $3{\cdot}3 \times 1{\cdot}25 = 4{\cdot}12$ dynes/cm. By equation (iii.) $\Gamma_{electrons} = \frac{4{\cdot}12}{0{\cdot}01} \times \frac{1}{9{\cdot}65 \times 10^{10}} = 4{\cdot}27 \times 10^{-10}$. The other values in column four were similarly calculated.

Table II.

E.M.F. in millivolts.	Difference in level of water-manometer in cm.	Difference.	$\Gamma_{electrons}$ in gr. equivalents per sq. cm. $\times 10^{-10}$.
10	3·2	...	...
15	4·9	3·3	−4·27
20	6·5	3·1	−4·01
25	8·0	2·9	−3·75
30	9·5	2·8	−3·62
35	10·8	2·6	−3·37
40	12·1	2·5	−3·24
45	13·3	2·5	−3·24
50	14·6	...	...

From fig. 4 it will be seen that the agreement for the solutions richer in mercurous sulphate (small E.M.F.'s) between the value of $\Gamma_{\text{electrons}}$, calculated with the aid of Gibbs' adsorption equation (or Lippmann's equation) and the "Nernst ionic transfer," directly observed at a contracting interface leaves nothing to be desired. The values for more dilute solutions (not given in the tables) show a discrepancy, increasing with the E.M.F., and probably due to the rate of diffusion of mercurous ions being insufficient to bring the tops to equilibrium before entering the downward flowing stream. Since the concentration of mercurous ions

Fig. 4.



decreases ten-fold for each 29 millivolts, we should expect the observed adsorption to fall off very rapidly with increasing E.M.F. were the ions discharged into the lower stream equal to those which diffused up to and were deposited upon the drop during its formation and fall in the upper stream. The fact that when the concentration is just too small to effect equilibrium, the subsequent decrease in the amount removed does not approach ten-fold with an increase of 29 millivolts in the E.M.F., is additional proof that the surface concentration of electrons set up at an expanding mercury surface is not entirely due to mercurous ions diffusing up to the surface, but is in part due to the production of mercurous ions by the chemical action of the acid on the expanding surface.

If this explanation for the discrepancy at the larger E.M.F.'s be accepted these experiments, besides giving a quantitative measure of the "Nernst ionic transfer," constitute an exact quantitative verification of an expression derived by the application of Gibbs' adsorption equation* by confirming the conclusions of the last section.

§ 4. *Conclusion.*

These experiments may alternatively be taken as affording a measure of the quantity of mercurous sulphate which must be removed from a solution in contact with mercury when the interface contracts by unit area in order to maintain the mercurous sulphate concentration in the solution unaltered†, and as thus confirming the conclusion derived by Warburg from Gibbs's adsorption equation that this is the electrochemical equivalent of ϵ of Lippmann's equation. It has already been observed that a surface charge can be formed by the retreat of electrons from the surface, but it is evident that this process can alternatively be regarded as a flux of electricity *across* the interface, which produces an equivalent quantity of mercurous sulphate in accordance with Faraday's laws. It must therefore be concluded that on increasing the area either a flux of electricity must pass across the interface, or an equivalent amount of mercurous sulphate must diffuse up to it from the solution (or be produced there by chemical action) in order to bring about equilibrium between the phases. In the experiments of Frumkin and those described above, the attainment of equilibrium by these two methods is studied, and they confirm quantitatively the conclusions obtained by applying Gibbs' adsorption equation. Neither these experiments nor the equation of Gibbs, however, give any clue as to why, from the standpoint of molecular mechanics, the presence of excess mercury salt at the interface is necessary for its equilibrium, nor yet as to the nature of the forces which hold it to the surface. They give no information as to the state of combination or dissociation of the mercurous sulphate when it has reached the interface, or its arrangement. Though its presence has evidently an influence

* Up to the present time the most exact verification of Gibbs' adsorption equation has been obtained by Donnan and Barker (Proc. Roy. Soc. A, lxxxv. p. 557 (1911)) for the adsorption of nonylic acid at a water–air interface. Discrepancies of the order of 50 per cent. were observed.

† In order to maintain a net zero charge in the system a number of sulphate ions equivalent to the number of mercurous ions must be simultaneously removed.

both on the electric moment of the interface, and on the surface-tension, no information can be obtained in this way about the precise molecular mechanisms at work *.

It is therefore apparent that the view of Euler that the adsorbed substance is held to the surface in the manner conceived of by Langmuir, that of Lewis that both ions and undissociated molecules are present at the interface, and that of Gouy that the surface-tension is affected by electrical repulsive forces in the Helmholtz boundary-layer, have no bearing on the question of the validity of Gibbs's adsorption equation. Any of these ideas may in the future be proved correct, partly correct, or incorrect, but in no case will the basis of the Gibbs equation be affected. The information which can be obtained by the use of Gibbs's method is strictly limited, but such as it is, it is entirely independent of questions of mechanism.

Summary.

1. Direct experimental measurements show that the amount of mercurous sulphate adsorbed at a mercury surface in contact with an electrolyte containing this salt corresponds quantitatively with that calculated from surface-tension measurements by Gibbs' adsorption equation.

2. The number of mercurous ions adsorbed at a freshly expanded interface is identified with the number of ions which on the Nernst theory of electrode potential are deposited on the mercury surface, and impart to it their charge.

3. This surface charge is equal to that calculated from the slope of the electrocapillary curve with the aid of Lippmann's equation, and regarded as a surface deficit of electrons may also be evaluated by a direct application of Gibbs' adsorption equation.

4. The surface charge may be set up by a retreat of

* Such information can only be obtained by inductive methods applied to the relation experimentally founded between the surface-tension, surface concentration, and other properties of the interface. It has been shown (Schofield and Rideal, Proc. Roy. Soc. A, cix. p. 57 (1925)) that in some cases surface films lower the surface-tension solely in virtue of their kinetic agitation. An accurately parabolic electrocapillary curve could be interpreted by supposing the adsorbed molecules each to have the same electric moment perpendicular to the interface, and to repel one another with a force varying inversely as the fourth power of their distance apart. It is hoped to take up this matter in more detail in the near future.

electrons from the surface, *i. e.*, by a flux of electricity across the interface.

5. This flux may in turn be regarded as producing at the surface, in accordance with Faraday's laws, the same quantity of mercurous sulphate as would be adsorbed from solution had no electric flux taken place.

In conclusion, I gladly take this opportunity of expressing my thanks to Dr. Rideal for constant help and advice during the progress of this work, and to the Board of Scientific and Industrial Research for a grant.

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LV. *Adsorption of Carbon Dioxide by Activated Coconut Charcoal.*

By H. Rowe, *B.Sc., Demonstrator in Physics, University College of the South-West of England, Exeter* *.

1. *Introduction.*

ADSORPTION with charcoal at low pressures must depend on the specific attraction of the solid for the gas molecules, and also upon the extent of the solid surface exposed to the gas, the attraction between the gas molecules being altogether negligible in comparison with that between the gas and the solid.

As the pressure is increased, the packing of the gas molecules upon the surface will become tighter, and a stage will be reached at which the gas molecules can accumulate further only by adhering to others already anchored. Then the mutual molecular attraction will become a factor of importance, and eventually, as the pressure becomes such as to bring the outside gas near to liquefaction, the adsorption of gas molecules will proceed at an intensified rate, filling the capillaries in the order of their fineness,

The largest capillaries of charcoal can be seen under the microscope, and, on an average, are 10^{-2} mm. in diameter †, or about 13,000 times the diameter of a nitrogen or hydrogen molecule. Lamb, Wilson and Chaney ‡ estimated the average diameter of the pores of activated charcoal, including the finest with the coarsest openings, to be about 5×10^{-6} mm., which is less than 7 times the diameter of the gas molecule. Lowry and Hulett § calculated the mean diameter of the capillaries, and found it varied between $2{\cdot}8\times10^{-6}$ mm. and $9{\cdot}2\times10^{-6}$ mm., the surfaces of the various charcoals ranging from 160 sq. metres to 436 sq. metres per gram of charcoal. It may be inferred from these figures that the greater part of the internal gaseous space of an efficient adsorbent consists of passages that are not much larger than the gas molecule.

In order to explain the phenomenon of adsorption several theories have been suggested, some of which will now be briefly considered.

1. Chemical combination. A theory of chemical combination has been brought forward in order to account

* Communicated by Prof. F. H. Newman, D.Sc., A.R.C.S.

† See H. Briggs, Proc. Roy. Soc. A. vol. c. p. 88 (1921).

‡ Journ. Indust. Eng. Chem. xi. p. 420 (1919).

§ Journ. Amer. Chem. Soc. xlii. p. 1408 (1920).

for the large amount of heat generated during the adsorption process.

2. Solid solution. This theory, accepted by Miss Homfray * as being the most consistent with her results, contemplates the actual penetration of the gas into the charcoal, the concentration being constant throughout the mass of the charcoal.

3. Solid condensation. This third theory—which accounts for the large amounts of gas adsorbed with a small quantity of charcoal better than the two theories given above—assumes that the gas is condensed upon the charcoal surface. This theory resulted from the fact that in early experiments the easily liquefied gases were always adsorbed to a great extent, and the investigators were led to believe that the adsorbed gas was condensed by the charcoal.

McBain †, as a result of his experiments with hydrogen and charcoal, considers that two processes occur. A condensation of gas on the charcoal surface is completed within two or three minutes, and a solid solution is formed by a slow diffusion—which may take more than 24 hours for completion—into the interior of the charcoal.

Langmuir ‡ has suggested a theory which in many respects is an elaboration of the solid solution and solid condensation theories. According to his theory, a gas molecule approaching a solid surface comes into the field of force of the atoms of the solid, and in general these gas molecules condense on the surface no matter what the temperature may be. At the same time, evaporation, the rate of which depends on the temperature, comes into play. Adsorption is a direct consequence of a time lag between condensation and subsequent evaporation. The adsorbed layer, according to Langmuir, does not exceed one molecule or, at the most, a few molecules in thickness. In order to account for the large volume of gas adsorbed by charcoal and other substances, he assumes that such substances present a much greater surface area than is apparent.

When plotting the relation between equilibrium pressure and gas adsorbed the resulting curve is always continuous, and is characteristic of a continuous series of solid solutions. No definite compound is formed and, usually, equilibrium is reached fairly rapidly—an argument, although by no means a conclusive one, against the existence of a solid solution.

* *Zeits. Phys. Chem.* lxxiv. p. 129 (1910).
† Phil. Mag. xviii. p. 916 (1909).
‡ Phys. Rev. viii. p. 149 (1916).

While the experiments on gaseous adsorption by charcoal show conclusively that the surface phenomena are important, there is also the possibility that a solid solution may be formed.

In the majority of cases the intermingling phenomena that constitute sorption have not been disentangled or even experimentally identified. From a theoretical point of view true adsorption, *i. e.* surface condensation, or the difference in concentration of the gas at the surface and within the bulk of the gas, attracts by far the most attention. Yet the phenomena of absorption or true solution in a solid are also of interest, and frequently the chemical reactions that ensue are of decisive importance, as for example in the case of catalysts.

It is important to insist on the distinction between the different factors because time relationships of adsorption and of absorption and again of chemical reaction are found to be widely different. The laws governing the amounts of gas sorbed by these processes also differ, but this is of less importance because when adsorption is present it sufficiently influences the net result so that the latter is represented by an adsorption equation.

True adsorption is nearly instantaneous. Any lag is at present accounted for by the time required for the dissipation of the heat evolved, or by the comparative inaccessibility of a portion of the surface of a porous adsorbing agent. On the other hand, absorption, or solid solution, may be expected to follow Fick's diffusion law which requires that it should commence with a very high velocity for the first few moments but rapidly fall off with time, and, theoretically, require infinite time for perfect equilibrium to be attained.

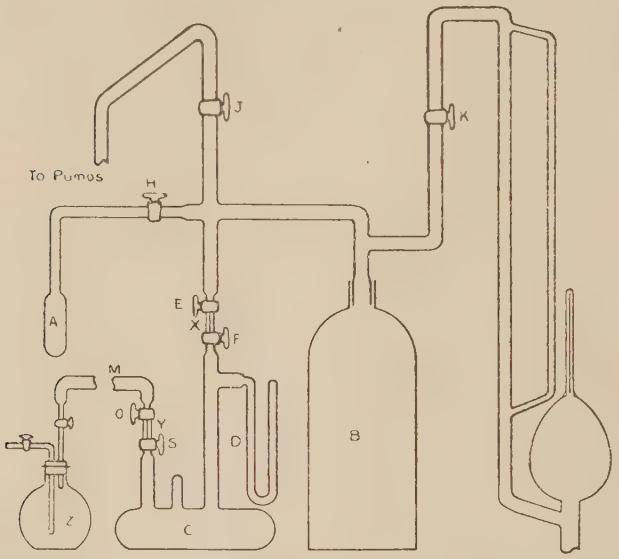
While performing experiments to determine the amount of carbon dioxide adsorbed by activated coconut charcoal *, it was noted that at very low pressures this gas required a considerable time to attain equilibrium; rapid adsorption took place during the first few minutes but was followed by slow absorption during the succeeding 24 hours. Most of the gas was adsorbed during the first stage, and the slow absorption that followed did not materially affect the volume taken up, but the final pressure attained depended primarily on the time during which the gas was in contact with the charcoal. This effect has been studied and the results obtained are given below.

* See H. Rowe, Phil. Mag. i. p. 109 (1926).

2. *Experimental Arrangement.*

The apparatus used in carrying out the experiments (fig. 1) was similar to that used for measuring the amounts of various gases adsorbed by activated charcoal at very low pressures *.

Fig. 1.



The coconut charcoal had been activated by the steam process, but before use it was reactivated by the "air-oxidation" treatment. This was effected by placing a shallow layer of the charcoal in a silica tube, open at both ends, and having an electric heating coil wound round it. The charcoal was heated to 450° C. for half-an-hour and air blown over its surface from time to time. A sample that had been used previously to measure the adsorption of carbon monoxide was employed to determine the rate of adsorption of carbon dioxide. This sample was completely outgassed by heating to 450° C. for 8 hours, the mercury-vapour pump backed by an oil pump working continuously to remove any gases liberated during this outgassing. The charcoal was tested for complete outgassing by allowing it to cool, the tap H being closed and the system being at a pressure less than 10^{-5} mm. † The charcoal was then

* *Loc. cit.*

† Pressures are expressed in mm. of mercury.

reheated to 450° C. for half-an-hour with the tap H open, the pumps being disconnected, and if no increase in pressure resulted it could be safely assumed that outgassing was complete.

Carbon dioxide was prepared by the action of pure hydrochloric acid on freshly boiled air-free marble in a Wolff bottle, and after passing over calcium chloride and phosphorus pentoxide to remove the excess of water-vapour it entered a small bulb Z having taps on the inlet and outlet tubes. A rapid stream of carbon dioxide was passed through the bulb for two hours, before closing the taps, to ensure the complete removal of atmospheric gases. The bulb Z containing the gas to be used was sealed to M and the whole of the apparatus exhausted to a pressure below 10^{-5} mm. Tap F was then closed and gas from Z admitted to the reservoir C by alternately opening and closing the taps O and S. In this way the gas pressure in C was raised to a convenient value.

The actual rate of adsorption of carbon dioxide was measured in the following manner. After the charcoal had been completely outgassed and the high vacuum side exhausted to 10^{-5} mm., tap H was closed and the pumps shut off. The gas was then admitted to the high vacuum side from the reservoir C by opening and closing taps E and F, so that the small volumes of gas trapped between these taps could be allowed to enter the high vacuum side. Sufficient gas was admitted to bring the pressure to any desired value, and after a period of 30 minutes during which equilibrium was attained, the pressure was noted on a McLeod gauge. Tap H was then opened and the pressure measured at stated intervals of time, the time of opening the tap H being taken as zero. After carrying out one series of readings the charcoal was completely outgassed by heating to 450° C. for 12 hours, and a new series of readings taken commencing at a different initial pressure. Great care was taken that the time and temperature were the same in all the experiments, so that the initial condition of the charcoal was as nearly as possible the same in all the experiments. The air temperature was read at one hour intervals and the average value noted. Throughout all the experiments its mean value was 20° C.

3. *Experimental Results,*

In all, six experiments were made at various initial pressures ranging from 2×10^{-2} mm. to $1{\cdot}5 \times 10^{-1}$ mm.

The results obtained are given in Table I., where t is

TABLE I.—Rate of Adsorption of Carbon Dioxide at 20° C.

Experiment 1.			Experiment 2.		
t.	*p.*	*q.*	*t.*	*p.*	*q.*
		c.c.			c.c.
0 min.	$36{\cdot}97\times10^{-3}$ mm.	0	0 min.	$92{\cdot}61\times10^{-3}$ mm.	0
2	24·93	6·506	2	59·78	17·76
15	3·494	18·11	15	15·33	41·05
30	1·742	19·06	30	11·46	43·91
60	1·349	19·27	60	9·607	44·91
120	1·161	19·37	120	7·652	45·98
360	1·158	19·38	360	5·118	47·38
1440	1·134	19·39	1440	4·178	47·86

Experiment 3.			Experiment 4.		
t.	*p.*	*q.*	*t.*	*p.*	*q.*
		c.c.			c.c.
0 min.	$141{\cdot}8\times10^{-3}$ mm.	0	0 min.	$113{\cdot}8\times10^{-3}$ mm.	0
2	87·36	29·48	2	74·97	21·12
15	26·56	62·38	15	23·85	48·59
30	22·20	64·74	30	18·26	51·70
60	19·54	66·19	60	15·41	53·25
90	18·09	66·97	90	13·93	54·04
120	17·19	67·45	180	11·69	55·26
240	14·86	68·73	300	9·630	56·37
1140	9·82	71·45	1080	6·149	58·25
1440	9·50	71·63	1440	5·758	58·46

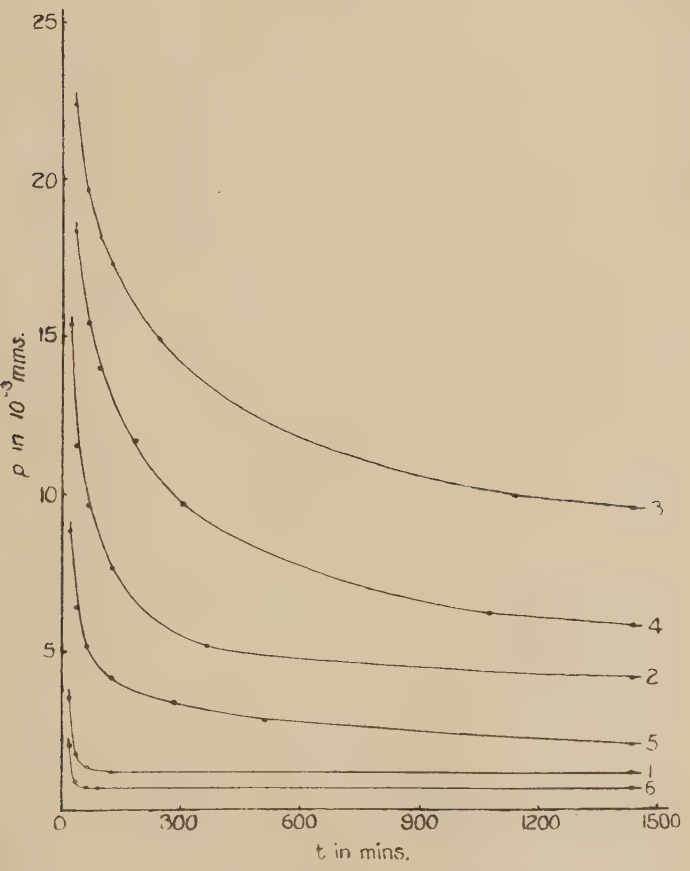
Experiment 5.			Experiment 6.		
t.	*p.*	*q.*	*t.*	*p.*	*q.*
		c.c.			c.c.
0 min.	$63{\cdot}38\times10^{-3}$ mm.	0	0 min.	$24{\cdot}67\times10^{-3}$ mm.	0
2	40·26	12·51	2	16·81	4·253
15	8·814	29·53	15	2·065	12·23
30	6·306	30·89	30	0·873	12·88
60	5·1	31·53	60	0·702	12·97
120	4·108	32·07	90	0·695	12·97
280	3·346	32·49	930	0·695	12·97
510	2·701	32·84	1440	0·695	12·97
1440	1·966	33·24			

the time in minutes, p is the pressure in mm., and q the quantity of gas adsorbed per gram of charcoal, expressed in c.c. at 1 mm. pressure and 20° C., is given by

$$q = \frac{V}{m}(p_0 - p),$$

where V = volume of high vacuum side = 3160 c.c.
m = mass of charcoal = 5·84 grms.
p_0 = initial pressure in mm.

Fig. 2.



Rate of Adsorption of CO_2 at Various Pressures.
Charcoal completely outgassed.

The graphical relation between pressure and time is shown in fig. 2.

An examination of the curves shows that as the initial and equilibrium pressures increase the time required for equilibrium to be attained becomes greater. The curves consist of two distinct portions, one part being almost vertical and the other tending to a horizontal direction. There is no sudden discontinuity in these parts, but they are joined by a smooth curve. Undoubtedly the rapid lowering of pressure with time that occurs in the first 30 minutes, and is represented by the almost vertical portion of the curves, is due primarily to *adsorption* forces, while the horizontal portion of the curves must be attributed, if McBain's theory is correct, to an *absorption* process taking place. *Absorption* follows a similar law to Fick's diffusion law. *i. e.* it is of exponential form, rapidly decreasing with time, but *adsorption* occurs so rapidly that it completely masks any *absorption* that may be present, and until *adsorption* has ceased the function of *absorption* cannot be detected. If $\log p/p_0$ is plotted against t for the various results it is found that for the portion between $t=60$ and 1440 minutes a straight line is obtained, thus showing that the lowering of pressure over this time interval is due solely to *absorption* forces.

The process of *absorption* must depend not only on the pressure of the gas outside the charcoal but also on the concentration within the charcoal, for *absorption* consists of the passing of gas into the finer capillaries of the charcoal after the coarser ones have been filled by *adsorption* processes. The gas concentration in the coarser capilliaries is then renewed by the *adsorption* of gas from the outside, and this continues until equilibrium is attained. In this respect *absorption* does not follow exactly the diffusion law, for experiment indicates that it reaches a limit in a measurable time, whereas the diffusion law states that infinite time is required for equilibrium to be attained.

From Table I., Experiment 6, it will be noted that the equilibrium pressure is attained after an interval of one hour, and that part of the curve shown in fig. 2 No. 6 which refers to *absorption* is represented by a horizontal straight line. It is inferred from this that below $0{\cdot}70 \times 10^{-3}$ mm. there is no *absorption* ; all gas within the sorbate being held by *adsorption* forces. The time required for this *adsorption* effect to be complete depends upon various factors. The actual rate of *adsorption* depends upon the dimensions of the apparatus, since at the very low pressures employed the mean free path of the gas molecules

is comparable with the dimensions of the apparatus, and a definite time will be required for the gas molecules to diffuse from the main volume to the charcoal bulb, where they replace those molecules of gas that have been absorbed. With the apparatus used *adsorption* was complete after 60 minutes approximately.

Investigations on the adsorptive capacity of charcoal for carbon dioxide, the charcoal containing some adsorbed gas, were made and the results are given in Table II.

Table II.

Rate of Adsorption of Carbon Dioxide at 15° C.

Experiment 1.

Initial conditions: Charcoal contained 36·32 c.c.—at 1 mm. pressure and 15° C.—per gram at an equilibrium pressure of $1{\cdot}745\times10^{-3}$ mm.

t.	*p.*	*q.*
0 min.	$18{\cdot}65\times10^{-3}$ mm.	0 c.c.
5	9·537	4·865
30	6·387	6·549
90	5·532	7·004
210	4·842	7·372
330	4·217	7·715
450	3·835	7·912
1440	2·515	8·614

Experiment 2.

Initial conditions: Charcoal contained 44·93 c.c.—at 1 mm. pressure and 15° C.—per gram at an equilibrium pressure of $2{\cdot}515\times10^{-3}$ mm.

t.	*p.*	*q.*
0 min.	$24{\cdot}97\times10^{-3}$ mm.	0 c.c.
5	13·29	6·210
30	9·764	8·108
60	9·312	8·351
150	8·416	8·831
270	7·561	9·283
390	7·100	9·532
510	6·444	9·881
1440	4·494	10·92

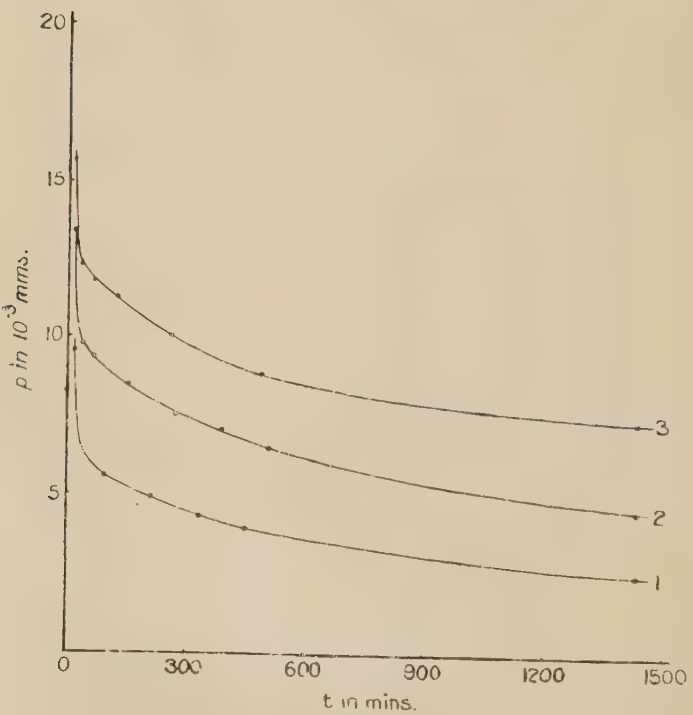
TABLE II. (*continued*).

Experiment 3.

Initial Conditions: Charcoal contained 56·10 c.c.—at 1 mm. pressure and 15° C.—at an equilibrium pressure of $4{\cdot}250 \times 10^{-3}$ mm.

t.	*p*.	*q*.
0 min.	$26{\cdot}69 \times 10^{-3}$ mm.	0 c.c.
5	15·52	5·964
30	12·27	7·703
60	11·77	7·968
120	11·22	8·258
260	10·01	8·902
360	9·165	9·354
490	8·840	9·528
1440	7·310	10·35

Fig. 3.



Rate of Adsorption of CO_2 at Various Pressures.
Charcoal not completely outgassed.

The results given in Table II. have been plotted and are shown in fig. 3. Considering these curves it will be noted

that they are similar to those given in fig. 2, but the *absorption* portion is more pronounced. Owing to the fact that the charcoal already contains some gas the quantity adsorbed from the surrounding gas will be considerably less and adsorption takes place very rapidly, so that after an interval of 15 minutes the *adsorption* process fails to mask the *absorption* phenomenon.

4. *Discussion.*

If *absorption* depends on the concentration of the gas in the charcoal, then it is quite possible that there will be a limiting value of this concentration below which *absorption* cannot take place. According to Langmuir * the first process in sorption is the formation of a monomolecular film on the surface of the sorbate. It is highly improbable that this is removed by *absorption* forces, and the presence of this film would account for no *absorption* taking place in Experiment 6 and very little in Experiment 1. Accordingly a value in the region of 13–16 c.c.—measured at 1 mm. pressure and 20° C.—may be taken as the limiting value of the gas concentration in the charcoal below which *absorption* cannot occur.

In general it is recognized that both *adsorption* and *absorption* commence simultaneously when outgassed charcoal is placed in contact with a gas, but if the above view is accepted then it must be inferred that though *adsorption* begins immediately, *absorption* will only commence after this definite concentration has been reached. At very high initial pressures this concentration would be attained almost immediately, so that for all practical purposes the two processas do commence at one and the same time at high pressures.

In Experiments 1 and 6, one-third of the total quantity sorbed is taken up in the first two minutes, and in each case this quantity is less than the minimum quantity adsorbed, but in the other experiments more than one-third is taken up in the same time and is, in each case, always greater than the minimum value. This fact seems to indicate that both processes occur at higher pressures, but *adsorption* only is the determining factor at very low pressures.

No rational expression for the variation in the rate of sorption described above has yet appeared. In fact, even an empirical analytical expression has not been formulated. The phenomena here described are of such complexity that it seems desirable to simplify experimental conditions and to secure more data before attempting to express a theory.

* Phys. Rev. viii. p. 149 (1916).

5. *Summary.*

1. While investigating the adsorptive capacity of activated coconut charcoal for carbon dioxide at very low pressures it was found that time effects came into operation, and a definite time was required for equilibrium pressure to be attained.

2. The rate of *adsorption* of carbon dioxide by outgassed charcoal at various initial pressures was measured.

3. It was found that in general *adsorption* and *absorption* processes were both present, but that below a definite equilibrium pressure, and definite concentration of the gas in the charcoal, *adsorption* alone was operative.

4. *Absorption* does not begin at the same time as *adsorption* but only when the concentration of the gas in the charcoal has reached this limiting value.

In conclusion the author wishes to express his sincere thanks to Prof. F. H. Newman for suggesting this branch of research and for the keen interest he has taken and the helpful suggestions made throughout.

LVI. *On the "Hypothetical Infinite Population" of Theoretical Statistics.* *By* W. Burnside, F.R.S. *

In a memoir on the Mathematical Foundation of Theoretical Statistics (Phil. Trans. vol. ccxxii.), Mr. R. A. Fisher, having stated that the object of statistical methods is the reduction of data, goes on (p. 311) :

"This object is accomplished by constructing a hypothetical infinite population, of which the actual data are regarded as constituting a random sample. The law of distribution of this hypothetical population is specified by relatively few parameters, which are sufficient to describe it exhaustively in respect of all qualities under discussion."

It is essential that the conception conveyed by the phrase "hypothetical infinite population," which is here introduced as one of the bases of theoretical statistics, should be the same for all who make use of it. Beyond the passage quoted above, nothing further occurs in Mr. Fisher's memoir to give precision to this conception. Readers of the memoir are thus thrown back upon the quoted passage to form their own conception of a "hypothetical infinite population."

* Communicated by the Author.

Now a statistical table, abstractly considered, consists of a finite number of distinct individuals, classified in respect of a finite number of classes. The simplest possible form of such a table will consist in the statement that in a collection of a finite number N of distinct individuals, N_A belong to class A, and the remaining $N - N_A$ do not belong to class A. Of what "hypothetical infinite populations" can this collection be regarded as a random sample? In the first place the "population" must consist of individuals, each two of which can be distinguished from each other, since this is a property of a random sample; and for the same reason, it must be known with respect to each individual of the "population" whether it does or does not belong to class A.

The first sentence in the passage quoted then leads to the conclusion that in this simplest case the "hypothetical infinite population" is a collection of distinct individuals which is classified in respect of class A.

It is less easy to be sure as to what is implied in regard to the "population" by the second sentence of the passage quoted. In this simplest case the quality under discussion is belonging or not belonging to class A. In the sample N_A/N of the individuals composing it belong to class A. This fraction is the frequency (or frequency-ratio) of individuals belonging to class A in the sample. It would seem that the most probable meaning of the second sentence in the passage quoted is that there is a proper fraction f which gives the same information with respect to the "hypothetical infinite population" that the fraction N_A/N gives with respect to the sample. The assumption that such a fraction as f exists is of the nature of an hypothesis, since a frequency-ratio is originally defined in connexion with a finite collection of individuals. This may account for the use of the word hypothetical in describing the population.

During the last thirty years there has been a large amount of valuable work in connexion with the properties of, and the relations between, collections of distinct individuals. Among the results which command the assent of all mathematicians are the following:—

With regard to a collection of distinct individuals, there are the following mutually exclusive possibilities. Either

(i.) it can be counted and the counting terminates; or

(ii.) it can be counted and the counting does not terminate; or

(iii.) it cannot be counted.

Further, between the individuals of any two collections which come under head (ii.) a one-to-one correspondence can be set up.

If a "hypothetical infinite population" comes under head (i.), it can only be said that the word "infinite" in its description has been unfortunately chosen. It, like the sample drawn from it, consists of a finite number of distinct individuals.

If a "hypothetical infinite population" comes under head (ii.), a one-to-one correspondence can be set up between the individuals constituting it and the collection of all positive integers. In this case the question whether the frequency-ratio of a class in "hypothetical infinite population" has any definite meaning may be replaced by the question whether the frequency-ratio of a specified class of integers in the collection of all integers has a definite meaning.

Now a specified class of integers can certainly be counted and there are the two alternatives that the counting (i.) terminates, (ii.) does not terminate. In the first case the specified class consists of a finite number N of integers. If a finite collection of integers is formed by combining with the N integers of the specified class M integers which do not belong to the class, the frequency-ratio of the specified class in this finite collection is $N/(N+M)$. No matter how the M integers are chosen, this fraction approaches the limit zero as the number M is taken larger and larger. It may be said then, in a quite definite sense, that when the specified class consists of a finite number of integers the frequency-ratio of the class in the totality of integers is zero. The statement that the frequency-ratio of a specified class of integers is zero does not, however, imply, as it would in dealing with a finite collection, that there are no individuals in the class. All that can be inferred is that if there are individuals in the class their number is finite.

Suppose now in the second case that the counting of the specified class does not terminate. A particular illustration of a class of this kind is the class of integers which are divisible by 7. If we suppose all integers arranged in order of magnitude and take the first N as a finite collection, the frequency-ratio of the specified class in the finite collection of N will, when N is large compared to 7, be very nearly $\frac{1}{7}$. If N is taken large enough it can be insured that the frequency-ratio of the specified class in the collection of N differs from $\frac{1}{7}$ by as small an amount as desired.

The order of magnitude is only one very particular way

of arranging all integers. Another arrangement is that indicated by

1, 7, 2, 14, 3, 21, 4, 28, 5, 35, 6, 42, 8, 49, 9, 56, 10, 63, 11, 70, 12, 77, 13, 84, 15, 91, ...

In this arrangement every integer occurs in one definite place, and no integer occurs twice.

If here the first N are taken as a finite collection, and N is large enough, the frequency-ratio of the specified class in the collection of N differs from $\frac{1}{2}$ by as small an amount as desired.

A precisely similar process may be used with any specified class which is not finite. The totality of integers may be arranged in a definite sequence in which each integer occurs once and no integer occurs twice, so that the first a do not belong to the specified class, the next b do, the next a do not, the next b do, and so on. If here the first N are taken as a finite collection, and N is large enough, the frequency-ratio of the specified class in the collection of N differs from $b/(a+b)$ by as small a quantity as desired.

What precedes justifies the following statement :—

When the " hypothetical infinite population " comes under head (ii.) it is not possible to obtain a unique value, other than zero, for the frequency-ratio of a specified class by calculating the frequency-ratio f_N of the class in a collection of N from the population, and determining the limit of f_N as N increases. This statement is not inconsistent with the further statement that " the frequency-ratio of a specified class in a hypothetical infinite population " is a phrase without meaning. The second sentence in the passage quoted from Mr. Fisher's memoir, if I have interpreted it correctly, implies that the author regards " the frequency-ratio of a specified class in a hypothetical infinite family " as a phrase with a perfectly definite meaning, and in any particular case a perfectly definite value. From this point of view the following question immediately suggests itself. What is the value of the frequency-ratio of the class of integers divisible by 7 in the collection of all integers, and what information does a knowledge of the value of this frequency-ratio give? So long as this question remains unanswered, it is a mere assumption to suppose that " the frequency-ratio of a specified class in a hypothetical infinite population " is a phrase with a definite meaning.

There remains the possibility that a "hypothetical infinite population" comes under head (iii.). If this is the case, the difficulties that arise in attaching a definite meaning and a definite value to the frequency-ratio of a specified class are certainly not less than in the case already considered, for it is not possible to approach such a collection directly from a collection which can be counted.

LVII. *The Vibrations of Rods and Shafts with Tension or End-Thrust.* *By* R. C. J. Howland, *M.A., M.Sc., University College, London* *.

1. *Introductory.*

THE determination of the whirling speeds of shafts subjected to an axial thrust or tension is of importance in the theory of some types of modern machinery, while a knowledge of the natural periods of vibration of rods in a state of longitudinal stress is needed when the stability of a framed structure is considered. The two problems are mathematically identical. In the general case, when the rod or shaft is not uniform or when it carries an unevenly distributed mass, the differential equation from which the critical states are to be determined cannot be integrated in a finite form.

For a rod or shaft without end-thrust or tension, a method for reducing the integration to a series of quadratures was given by Messrs. Cowley and Levy †. Their method solves the equation in a series in powers of a parameter which is a multiple of the square of the whirling speed or of the frequency. The method is essentially a particular application of the method of successive approximation which, in various forms, has been used at least since the time of Laplace. A general theory is given by Picard ‡ and repeated by Bateman §. Expansions in powers of a parameter occur in the theory of integral equations ‖. A solution of certain

* Communicated by the Author.

† "On a Method of Analysis suitable for the Differential Equations of Mathematical Physics," Phil. Mag. xli. April 1921.

‡ E. Picard, 'Traité d'Analyse,' t. ii. 2nd ed. p. 340 (1905).

§ H. Bateman, 'Differential Equations,' p. 245 (1918).

‖ See, for example, Whittaker & Watson, 'Modern Analysis,' 3rd ed. p. 213 (1920).

differential equations in a series in powers of parameters was given by Baker *, who traces his method back to Caqué † and Fuchs ‡. Caqué's solution of the general linear equation in terms of iterated functions obtained by a sequence of integrations has affinities to the method of the present paper §.

A special application of the method of Cowley and Levy to determine the whirling speeds of a shaft carrying concentrated masses was made by the present writer in a recent paper ‖. A theoretical deduction of Dunkerley's Rule was given and the magnitude of the error involved in the use of this rule was investigated.

In the present paper the same method is applied to the more general problem of a rod or shaft under axial force. By the assumption of a double series in powers of two parameters a solution is found which, involving only quadratures, is suitable for graphical or numerical calculation. The method is illustrated by applying it to a uniform shaft, and the results are compared with those given by an exact integration. An application to rods and shafts carrying concentrated masses is then made and the error in Dunkerley's Rule is calculated for a number of different end-thrusts and tensions. The method is both rigorous and general.

Only special cases of the general problem appear to have received attention previously. The vibrations of a uniform bar under tension were considered by Clebsch ¶, and the same analysis has been applied to the problem of whirling ** and to that of the stability of a rotating shaft under end-thrust ††. The vibrations of struts with several supports and uniform in each bay have been considered by Cowley and

* H. F. Baker, "On Certain Linear Differential Equations of Astronomical Interest," Phil. Trans. A, ccxvi. pp. 129–186 (1916).

† M. J. Caqué, "Méthode nouvelle pour l'intégration des équations différentielles linéaires," Liouville's Journal, 2nd ser. t. ix. pp. 185–222 (1864).

‡ Fuchs, *Ann. d. Mat.* 2nd ser. t. iv. p. 36.

§ *Cf.* also a series of papers by E. & F. Cosserat, *Comptes Rendus*, cxxvi. (1898) and cxxxiii. (1901).

‖ "The Whirling Speeds of Shafts Carrying Concentrated Masses," Phil. Mag. xlix. p. 1131 (1925).

¶ Clebsch, "Theorie der Elasticität fester Körper," Chap. iv. § 61, or in the French translation of de St. Venant, p. 480 gg. See also Rayleigh, 'Theory of Sound,' 2nd ed. p. 296.

** See, for example, Morley, 'Strength of Materials,' 5th ed. p. 464.

†† H. Mawson, "Struts and Tie-Rods in Motion," Proc. Inst. Mech. Eng. 1915, p. 463.

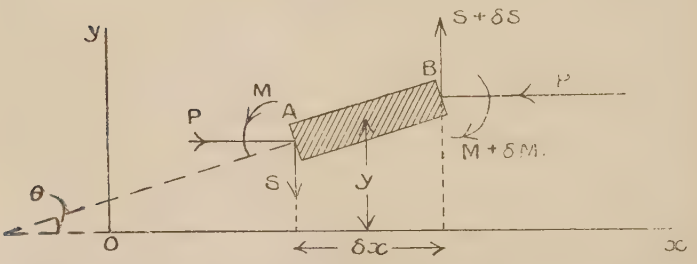
Levy*, using the general equations, and by Shôgenji†, using Rayleigh's approximate method. The whirling speed of a shaft axially loaded and carrying a central mass was considered by Melan ‡ by Ritz's minimum energy method. More recently Schwerin § has obtained interesting results in the same problem by using the full expression for the curvature of the shaft, thus extending the work of v. Mises ‖ on the shaft without end-thrust. But no general method for calculating the whirling speeds of non-uniform shafts or the vibration periods of non-uniform rods under axial forces appears to have been published.

2. *The Differential Equation.*

Consider a shaft specified as follows :—

Young's Modulus	E
Density of Material	ρ
Area of Cross-section	A
Second Moment of Cross-section ...	$I = Ak^2$
End-thrust	P
Angular Velocity	ω
Distance from a chosen end	x
Deflexion	y

Fig. 1.



Let M be the bending moment, S the stress resultant parallel to the axis of y; P, the stress resultant parallel to the axis of x, is constant.

* Cowley & Levy, "Vibration and Strength of Struts and Continuous Beams under End-Thrusts," Proc. Roy. Soc. A, vol. xcv. (1918).

† Shôgenji, "Approximate Calculation of the Natural Period of Rods," Mem. Coll. Eng. Kyushu, vol. iii. No. 3 (1924).

‡ H. Melan, "Kritische Drehzahlen von Wellen mit Längsbelastung," *Zeit. Oestr. Ing. u. Arch. Ver.* xliv. p. 45 (1917).

§ E. Schwerin, "Die Stabilität rotierender achsial belasteter Wellen," *Zeit. f. ang. Math. u. Mech.* v. p. 101 (1925).

‖ R. v. Mises, *Monatshefte f. Math. u. Phys.* 1911, p. 44.

Then the equations of motion of the element AB (fig. 1) are :—

(1) From acceleration parallel to y-axis,

$$\rho A\,\delta x\,(\ddot{y}-y\omega^2) = \delta S.$$

(2) From rate of change of angular momentum,

$$\rho A\,\delta x\,[k^2+(\tfrac{1}{2}\,\delta x)^2]\theta = \delta M + P\frac{dy}{dx}\,\delta x + S\,\delta x,$$

or, when $\delta x \to 0$,

$$\rho A(\ddot{y}-y\omega^2) = \frac{dS}{dx}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\rho I\frac{d^3y}{dt^2\,dx} = \frac{dM}{dx} + P\frac{dy}{dx} + S. \quad . \quad . \quad . \quad (2)$$

To these may be added the usual relation between curvature and bending moment,

$$M = EI\frac{d^2y}{dx^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Differentiating (2) with regard to x and substituting from (1) and (3) for $\dfrac{dS}{dx}$ and M, we have

$$\frac{d}{dx}\left(\rho I\frac{d^3y}{dx\,dt^2}\right) = \frac{d^2}{dx^2}\left(EI\frac{d^2y}{dx^2}\right) + P\frac{d^2y}{dx^2} + \rho A\left(\frac{d^2y}{dt^2} - y\omega^2\right), \quad (4)$$

where ρI, EI, ρA are, in general, functions of x.

If the rotating shaft executes vibrations of frequency σ, the equation becomes

$$\frac{d^2}{dx^2}\left(EI\frac{d^2y}{dx^2}\right) + 4\pi^2\sigma^2\frac{d}{dx}\left(\rho I\frac{dy}{dx}\right) + P\frac{d^2y}{dx^2} - \rho A(4\pi^2\sigma^2+\omega^2)y = 0. \quad . \quad (5)$$

For the case of a rod without rotation, we have $\omega^2=0$; while, for a shaft at one of its whirling speeds, one vibration frequency becomes zero and the equation is

$$\frac{d}{dx^2}\left(EI\frac{d^2y}{dx^2}\right) + 4\pi^2\sigma^2\frac{d}{dx}\left(\rho I\frac{dy}{dx}\right) + P\frac{d^2y}{dx^2} - \rho A\omega^2 y = 0. \quad (6)$$

The nature of the parameters involved is made clearer if

the coordinates are made non-dimensional. This is accomplished by using the transformation,

$$\left.\begin{aligned} x &= lx' \\ y &= ly' \\ \rho A &= \rho_0 A_0 f(x') \\ EI &= E_0 I_0 \phi(x') \\ \rho I &= \rho_0 I_0 \psi(x'), \end{aligned}\right\} \quad \ldots\ldots \quad (7)$$

where l is any fixed length and will be taken to be the whole length of the shaft, and ρ_0, A_0, E_0, I_0 are the values of ρ, A, E, I at some selected point, say the origin. Making this substitution and then dropping the dashes, we find

$$\frac{d^2}{dx^2}\left\{\phi(x)\frac{d^2y}{dx^2}\right\} + q^2\frac{d}{dx}\left\{\psi(x)\frac{dy}{dx}\right\} + p^2\frac{d^2y}{dx^2} - \theta^4 f(x)y = 0, \quad \ldots \quad (8)$$

in which

$$\left.\begin{aligned} q^2 &= \frac{\rho_0 l^2}{E_0}\cdot 4\pi^2\sigma^2, \\ p^2 &= \frac{Pl^2}{E_0 I_0}, \\ \theta^4 &= \frac{\rho_0 A_0 l^4}{E_0 I_0}(4\pi\sigma^2 + \omega^2); \end{aligned}\right\} \quad \ldots\ldots \quad (9)$$

q, p and θ are pure numbers, non-dimensional in mass, length and time, and (8) is expressed wholly in terms of non-dimensional quantities. When the shaft is in tension, p^2 is negative.

It is interesting to note that, in the case where ρI is constant, the only effect of the rotatory inertia term is to increase the effective end-thrust P. When $\sigma = 0$, *i. e.* for a steady deflexion at a whirling speed, this term disappears from the equation. In other cases, it is usually small and in what follows it will be neglected. The equation then takes the form

$$\frac{d^2}{dx^2}\left\{\phi(x)\frac{d^2y}{dx^2}\right\} + p^2\frac{d^2y}{dx^2} - \theta^4 f(x)y = 0, \quad \ldots \quad (10)$$

together with the end conditions

$$y = 0 \quad \text{when} \quad x = 0 \text{ or } 1,$$

$$\frac{d^2y}{dx^2} = 0 \quad \text{when} \quad x = 0 \text{ or } 1, \text{ (short bearing)},$$

or $$\frac{dy}{dx} = 0 \quad \text{when} \quad x = 0 \text{ or } 1, \text{ (long bearing)}.$$

In all the problems considered, it is required to find for what values of the parameters the equation has a non-zero solution. Usually p^2 is regarded as known and θ^4 is sought. The inverse problem is also of interest. Given θ^4 we may attempt to find p^2 and hence the critical values of the thrust under which the shaft will tend to buckle if, while rotating with a given angular velocity, it is subject to a forced vibration of known frequency. For such purposes a solution of (10) in a series in powers of the parameters p^2 and θ^4 is convenient.

3. *Solution by Quadratures.*

The required development may be found in a form involving only quadratures by the following method.

Let

$$y = \mathrm{A}y_1 + \mathrm{B}y_2 + \mathrm{C}y_3 + \mathrm{D}y_4 \quad . \quad . \quad . \quad . \quad (11)$$

be the complete primitive of the differential equation

$$\frac{d^2}{dx^2}\left\{\phi(x)\frac{d^2y}{dx^2}\right\} = 0,$$

and denote the integral operators

$$\int_0^x dx \int_0^x \frac{dx}{\phi(x)}$$

and $$\int_0^x dx \int_0^x \frac{dx}{\phi(x)} \int_0^x dx \int_0^x dx\, f(x)$$

by α and β respectively.

Then if (11) is taken as a first approximation to a solution of (10) and is substituted in the second and third terms of (10), a second approximation is obtained by integration in the form

$$\mathrm{A}\{y_1 + (\theta^4\beta - p^2\alpha)y_1\} + \mathrm{B}\{y_2 + (\theta^4\beta - p^2\alpha)y_2\} + \text{ etc.}$$

Repeating this process we obtain a third approximation,

$$\mathrm{A}\{y_1 + (\theta^4\beta - p^2\alpha)y_1 + (\theta^4\beta - p^2\alpha)^2 y_1\} + \mathrm{B}\{\ \ldots\ \} + \text{ etc.}$$

and so on.

It must be noted that, in developing a power $(\theta^4\beta - p^2\alpha)^r$ we have r^2 terms, since $\alpha\beta$ and $\beta\alpha$ are distinct.

The above process leads to four infinite series of the type

$$y = y_n + (\theta^4\beta - p^2\alpha)y_n + (\theta^4\beta - p^2\alpha)^2 y_n + \text{etc.} \quad . \quad (12)$$

$n = 1, 2, 3, 4.$

It will now be verified that each series gives a solution of the differential equation. For, apply to y the operator

$$\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2},$$

assuming, for the moment, that it is legitimate to apply it term by term. Then, since

$$\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}y_n = 0$$

and

$$\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}(\theta^4\beta - p^2\alpha) \equiv \theta^4 - p^2\frac{d^2}{dx^2},$$

we have at once

$$\left(\frac{d^2}{dx^2}\phi(x)\frac{d^2}{dx^2}\right)y = \left(\theta^4 - p^2\frac{d^2}{dx^2}\right)[y_n + (\theta^4\beta - p^2\alpha)y_n + \ldots]$$

$$= \left(\theta^4 - p^2\frac{d^2}{dx^2}\right)y,$$

and the equation is formally satisfied.

This procedure will be justified if it can be proved that the result of term by term differentiation is uniformly convergent, *i. e.* that

$$\left(\theta^4 - p^2\frac{d^2}{dx^2}\right)y$$

is a uniformly convergent series.

Now $\phi(x)$ is a positive, bounded function in the interval $0 < x < 1$. If its lower bound is λ we may write

$$\left.\begin{aligned} y_1 &= 1, \\ 0 < y_2 &= x < 1, \\ 0 < y_3 &= \int_0^x dx \int_0^x \frac{dx}{\phi(x)} < \frac{1}{\lambda}\cdot\frac{x^2}{2} < \frac{1}{\lambda}, \\ 0 < y_4 &= \int_0^x dx \int_0^x \frac{x\,dx}{\phi(x)} < \frac{1}{\lambda}\,\frac{x^3}{3} < \frac{1}{\lambda}, \end{aligned}\right\} \quad . \quad . \quad (13)$$

so that all the functions y_1, y_2, y_3, y_4 are positive and bounded.

Again, $f(x)$ is a positive, bounded function in the interval considered. If μ be its upper bound and if $\psi(x)$ be *any* positive function having an upper bound K in the interval, it is evident that

$$0 < \beta\psi(x) \leq \frac{\mu K}{\lambda}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x dx$$

$$= \frac{\mu K}{\lambda} \cdot \frac{x^4}{\lfloor 4}$$

and

$$0 < \alpha \,.\, \psi(x) \leq \frac{K}{\lambda}\int_0^x dx \int_0^x dx$$

$$= \frac{K}{\lambda} \cdot \frac{x^2}{\lfloor 2}.$$

Thus

$$\left|(\theta^4\beta - p^2\alpha)\psi(x)\right| \leq \frac{K}{\lambda} \cdot \frac{x^2}{\lfloor 2}\left(p^2 + \frac{\mu\theta^4 x^2}{12}\right)$$

$$\leq K \frac{x^2}{\lfloor 2}\nu,$$

where $$\nu = \left(p^2 + \frac{\mu\theta^4}{12}\right) \cdot \frac{1}{\lambda}, \quad \text{since } x^2 \leq 1.$$

Again, we have, for $m \geq 2$,

$$0 < \beta \,.\, \frac{x^m}{\lfloor m} \leq \frac{\mu}{\lambda}\int_0^x dx \int_0^x dx \int_0^x dx \int_0^x \frac{x^m}{\lfloor m} dx$$

$$= \frac{\mu}{\lambda} \frac{x^{m+4}}{\lfloor m+4},$$

$$0 < \alpha \,.\, \frac{x^m}{\lfloor m} \leq \frac{1}{\lambda}\int_0^x dx \int_0^x \frac{x^m}{\lfloor m} dx$$

$$= \frac{1}{\lambda} \frac{x^{m+2}}{\lfloor m+2},$$

so that

$$\left|(\theta^4\beta - p^2\alpha) \,.\, \frac{x^m}{\lfloor m}\right| \leq \frac{1}{\lambda} \frac{x^{m+2}}{\lfloor m+2}\left(p^2 + \frac{\mu\theta^4 x^2}{(m+3)(m+4)}\right)$$

$$< \nu^2 \cdot \frac{x^{m+2}}{\lfloor m+2}.$$

Hence

$$\left|(\theta^4\beta - p^2\alpha)^2\psi(x)\right| \leq \mathrm{K}\nu\left|(\theta^4\beta - p^2\alpha)\frac{x^2}{\lfloor 2}\right|$$

$$< \mathrm{K}\nu^2\frac{x^4}{\lfloor 4};$$

$$\left|(\theta^4\beta - p^2\alpha)^3\psi(x)\right| < \mathrm{K}\nu^2\left|(\theta^4\beta - p^2\alpha)\cdot\frac{x^4}{\lfloor 4}\right|$$

$$< \mathrm{K}\nu^3\frac{x^6}{\lfloor 6};$$

and, generally,

$$\sum_{r=0}^{\infty}\left|(\theta^4\beta - p^2\alpha)^r\psi(x)\right|$$

$$< \mathrm{K}\left[1 + \frac{\nu x^2}{\lfloor 2} + \frac{\nu^2 x^4}{\lfloor 4} + \ldots\right],$$

a series which is absolutely and uniformly convergent for all values of ν and x.

Each of the series y is therefore absolutely and uniformly convergent. It follows easily that the series obtained by operating with

$$\theta^4 - p^2\frac{d^2}{dx^2}$$

is uniformly convergent. For, if the first term is omitted the remainder may be written

$$\left(\theta^4 - p^2\frac{d^2}{dx^2}\right)(\theta^4\beta - p^2\alpha)y$$

$$= \theta^4(\theta^4\beta - p^2\alpha)y + \frac{p^4}{\phi(x)}y - \frac{p^2\theta^4}{\phi(x)}\int_0^x dx\int_0^x dx\, f(x)y.$$

The first two terms give series which are obviously uniformly convergent in view of the preceding discussion. Also, if $\mathrm{R_N}$ be the remainder after N terms of the series

$$\int_0^x dx\int_0^x dx\, f(x)y,$$

and $\mathrm{R'_N}$ the remainder in the series y, we can assign N, independently of x, so that

$$\mathrm{R'_N} < \frac{e}{\mu},$$

where μ, as before, is the upper bound of $f(x)$ and e is

arbitrarily small. Then

$$\begin{aligned} R_N &< \frac{e}{\mu}\int_0^x dx \int_0^x f(x)\,dx \\ &< e\int_0^x dx \int_0^x dx = e\frac{x^2}{2} < e, \end{aligned}$$

so that the integrated series is also uniformly convergent, as is also the series

$$\left(\theta^4 - p^2\frac{d^2}{dx^2}\right)y.$$

This justifies the procedure previously adopted and shows that the solution is valid for all values of the parameters.

The above argument needs a little modification when, as occurs in a later application, the shaft carries concentrated masses, since $f(x)$ has then infinities in the range and no upper bound can be assigned to it. Suppose, for example, that $f(x)$ has infinities at $x = a_k$, $k = 1, 2, 3, \ldots$, and that

$$\lim_{\epsilon \to 0} \int_{a_k-\epsilon}^{a_k+\epsilon} f(x)\,dx = \mu_k.$$

Then if μ be the greatest value of $f(x)$ in the intervals between the infinities and if $\psi(x)$ be any continuous, bounded function,

$$\left|\int_0^x f(x)\,\psi(x)\,dx\right| \leq \mu\int_0^x |\psi(x)|\,dx + \Sigma|\mu_k||\psi(a_k)|,$$

the summation extending to all values of a_k less than x. Writing

$$|\mu_1||\psi(a_1)| = s_1,$$
$$|\mu_1||\psi(a_1)| + |\mu_2||\psi(a_2)| = s_2,$$

and so on, we have

$0 < x < a_1$ $\quad \left|\int_0^x f(x)\,\psi(x)\,dx\right| \leq \mu\int_0^x |\psi(x)|\,dx,$

$a_1 < x < a_2$ $\quad \left|\int_0^x f(x)\,\psi(x)\,dx\right| \leq \mu\int_0^x |\psi(x)|\,dx + s_1,$

$a_i < x < a_{i+1}$ $\quad \left|\int_0^x f(x)\,\psi(x)\,dx\right| \leq \mu\int_0^x |\psi(x)|\,dx + s_i$

$$\leq \mu_i\int_0^x |\psi(x)|\,dx,$$

where $$\mu_i = \mu + \frac{s_i}{\int_0^{a_i} |\psi(x)|\,dx}.$$

Now let M be the greatest of the numbers $\mu_1, \mu_2, \mu_3, \ldots \mu_i, \ldots$. Then for every value of x in the range $0 < x < 1$,

$$\left| \int_0^x f(x)\,\psi(x)\,dx \right| \leq \mathrm{M} \int_0^x |\psi(x)|\,dx,$$

and M replaces μ in the foregoing proof of convergence, which otherwise stands without change.

In the type of application that follows, p is regarded as known and the values of θ are sought. For this purpose it is often convenient to rearrange the series in powers of θ. The general solution of (10) then takes the form

$$y = \mathrm{A}f_1(x) + \mathrm{B}f_2(x) + \mathrm{C}f_3(x) + \mathrm{D}f_4(x), \quad . \quad (14)$$

where

$$\begin{aligned} f_n(x) = y_n &+ \theta^4[\beta - p^2(\beta\alpha + \alpha\beta) + p^4(\beta\alpha^2 + \alpha\beta\alpha + \alpha^2\beta) \\ &\quad - \text{etc.}]\,y_n \\ &+ \theta^8[\beta^2 - p^2(\beta^2\alpha + \beta\alpha\beta + \alpha\beta^2) + \text{etc.}]\,y_n \\ &+ \ldots \text{ad inf.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15) \end{aligned}$$

and y_1, y_2, y_3, y_4 have the values given in (13).

The solution is expressed entirely in terms of quadratures and is thus suited to graphical or numerical methods of calculation.

4. *Uniform Shaft Without Attached Masses.*

When the shaft is uniform the integrations in (15) become very simple. Since an exact solution of (10) is also available in this case, a good opportunity is given for illustrating the accuracy of the present method and the types of error involved in truncating the series at different points.

When $f(x) = \phi(x) = 1$, the operators α and β reduce to simple repeated integrations with regard to x. It will be convenient to have a special notation for such integrations. The following will be used :—

$$\left.\begin{aligned} \mathrm{S}\ \psi(x) &\equiv \int_0^x \psi(x)\,dx, \\ \mathrm{S}^2\,\psi(x) &\equiv \int_0^x dx \int_0^x \psi(x)\,dx, \\ &\text{and so on.} \\ \mathrm{S}_1\,\psi(x) &\equiv \int_0^1 \psi(x)\,dx, \\ \mathrm{S}_1{}^2\psi(x) &\equiv \int_0^1 dx \int_0^x \psi(x)\,dx, \\ &\text{etc.} \end{aligned}\right\} \quad . \quad . \quad . \quad (16)$$

To avoid the use of additional brackets, it will be supposed that S operates upon all that follows it until a plus or minus sign is reached.

Then, in the problem considered, we have

$$y_1 = 1, \quad y_2 = \mathrm{S}.1, \quad y_3 = \mathrm{S}^2.1, \quad y_4 = \mathrm{S}^3.1, \quad (17)$$

$$\alpha \equiv \mathrm{S}^2, \quad \beta \equiv \mathrm{S}^4,$$

and hence

$$\begin{aligned} f_n(x) = {} & y_n + \theta^4[\mathrm{S}^4 - 2p^2\mathrm{S}^6 + 3p^4\mathrm{S}^8 + \ldots]y_n \\ & + \theta^8[\mathrm{S}^8 - 3p^2\mathrm{S}^{10} + 6p^4\mathrm{S}^{12} - \ldots]y_n \\ & + \text{etc.} \end{aligned}$$

It is easily seen that this formula may also be written

$$f_n(x) = \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (-1)^u \frac{\lfloor u+v}{\lfloor u \rfloor v} p^{2u} \theta^{4v} \mathrm{S}^{2u+4v} . y_n. \quad . \quad (18)$$

So far, the result applies to any shaft of uniform flexural rigidity, whether the distribution of mass is uniform or not. When the functions y_n have the special values (17) the complete solution is

$$y = \mathrm{A}f_1(x) + \mathrm{B}f_2(x) + \mathrm{C}f_3(x) + \mathrm{D}f_4(x),$$

where

$$f_n(x) = \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (-1)^u \frac{\lfloor u+v}{\lfloor u \rfloor v} \frac{x^{2u+4v+n-1}}{\lfloor 2u+4v+n-1} p^{2u} \theta^{4v}. \quad (19)$$

If the shaft has a short bearing at each end, the boundary conditions are

$$y = \frac{d^2y}{dx^2} = 0, \text{ when } x = 0 \text{ or } 1. \quad . \quad . \quad (20)$$

From (19) it is obvious that

$$\begin{aligned} & f_1(0) = 1, \qquad f_2(0) = f_3(0) = f_4(0) = 0, \\ & f_1''(0) = -p^2, \quad f_3''(0) = 1, \\ & f_2''(0) = f_4''(0) = 0. \end{aligned}$$

Hence

$$\begin{aligned} & \mathrm{A} = \mathrm{C} = 0, \\ & \mathrm{B}f_2(1) + \mathrm{D}f_4(1) = 0, \\ & \mathrm{B}f_2''(1) + \mathrm{D}f_4''(1) = 0, \end{aligned}$$

and the whirling speeds are given by

$$f_2(1)f_4''(1) = f_2''(1)f_4(1). \quad . \quad . \quad . \quad . \quad (21)$$

When the series in θ is continued as far as the terms in θ^8 and the results are substituted in (21), an equation for θ is obtained in the form

$$A\theta^4 = B + C\theta^8, \quad . \quad . \quad . \quad . \quad . \quad (22)$$

where A, B, C have the values shown in Table I.

The Euler thrust at which the shaft tends to buckle when at rest is given by $p^2=\pi^2$. In practice, the values of p^2 which we have to consider will be much less than this and it will be found that powers of p above the sixth are negligible on account of the smallness of their coefficients. The calculation of A, B, and C is then very simple. Even when p^2 is as great as 9 the convergence is rapid.

Table I.

	p^2.	A.	B.	C.
Tension	−4	·01466	1·8134	$10{\cdot}55\times10^{-6}$
	−3	·01370	1·5806	$10{\cdot}09\times10^{-6}$
	−2	·01279	1·3683	$9{\cdot}65\times10^{-6}$
	−1	·01193	1·1752	$9{\cdot}23\times10^{-6}$
	0	·01111	1·0000	$8{\cdot}82\times10^{-6}$
Thrust.....	1	·01033	0·8415	$8{\cdot}42\times10^{-6}$
	2	·00961	0·6985	$8{\cdot}02\times10^{-6}$
	3	·00892	0·5699	$7{\cdot}68\times10^{-6}$
	4	·00827	0·4546	$7{\cdot}33\times10^{-6}$
	5	·00765	0·3518	$6{\cdot}99\times10^{-6}$
	7	·00653	0·1798	$6{\cdot}36\times10^{-6}$
	9	·00553	0·0470	$5{\cdot}78\times10^{-6}$

From (22) the lowest value of θ^4 may be found by successive approximation. Thus

$$\theta_0^4 = \frac{B}{A},$$

$$\theta_1^4 = \theta_0^4 + \frac{C}{A}\theta_0^8,$$

$$\theta_2^4 = \theta_0^4 + \frac{C}{A}\theta_0^8 + 2\left(\frac{C}{A}\right)^2\theta_0^{12},$$

$$\theta_3^4 = \theta_0^4 + \frac{C}{A}\theta_0^8 + 2\left(\frac{C}{A}\right)^2\theta_0^{12} + 5\left(\frac{C}{A}\right)^3\theta_0^{16}.$$

The values of θ_0^4, θ_1^4, and θ_3^4 are given in Table II. Further approximation after θ_3^4 does not substantially alter the value

obtained and θ_3^4 may be taken as the final value of θ^4 given by (22).

TABLE II.

First, Second, and Final Approximations to θ^4.

	p^2.	θ_0^4.	θ_1^4.	θ_3^4.
Tension	−4	123·69	134·50	137·14
	−3	115·37	125·17	127·25
	−2	106·99	115·62	117·33
	−1	98·53	106·05	107·43
	0	90·00	96·43	97·50
Thrust	1	81·42	86·82	87·66
	2	72·69	77·11	77·79
	3	63·88	67·40	67·84
	4	54·99	57·67	57·96
	5	45·97	47·90	48·07
	7	27·54	28·28	28·33
	9	8·50	8·57	8·59

These results will now be compared with those given by the exact method. With the special values of $f(x)$ and $\phi(x)$ equation (5) becomes

$$\frac{d^4y}{dx^4} + p^2\frac{d^2y}{dx^2} = \theta^4 y, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

and the general solution is

$$y = A\cosh\alpha x + B\sinh\alpha x + C\cos\beta x + D\sin\beta x,$$

where

$$2\alpha^2 = \sqrt{p^4 + 4\theta^4} - p^2,$$

$$2\beta^2 = \sqrt{p^4 + 4\theta^4} + p^2.$$

The end conditions give

$$A = B = C = 0,$$

and

$$\sin\beta = 0.$$

From the last equation, the lowest whirling speed is to be found from

$$p^2 + \sqrt{p^4 + 4\theta^4} = 2\pi^2,$$

whence

$$\theta^4 = \pi^2(\pi^2 - p^2). \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Table III. shows the values of θ^4 given by (24) and the errors in the approximations θ_0^4, θ_1^4, and θ_3^4.

TABLE III.

	p^2.	$\pi^2(\pi^2-p^2)$.	Error in θ_0^4. per cent.	Error in θ_1^4. per cent.	Error in θ_3^4.
Tension	−4	136·89	9·5	1·93	Less than 0·2 per cent.
	−3	127·02	9·2	1·63	
	−2	117·15	8·8	1·46	
	−1	107·28	8·2	1·3	
	0	97·41	7·7	1·0	0·1 per cent.
Thrust.....	1	87·54	7·0	0·8	Less than 0·1 per cent.
	2	77·67	6·4	0·7	
	3	67·80	5·8	0·6	
	4	57·93	5·1	0·5	
	5	48·06	4·4	0·3	
	7	8·32	22·7	0·1	
	9	8·58	1·0	0·1	

Since in the case of whirling θ^4 contains ω^2 as a factor, the errors in ω^2 will be about half those in θ^4. It will be seen that the errors in the first approximation are all less than 5 per cent. The errors in the second approximation are very small, while the final approximation gives ω without appreciable error.

The inversion of Table II. by means of a graph will give the critical thrust at which the shaft tends to buckle when rotating with a given angular velocity and subjected to a forced vibration of given frequency.

Equation (22) may be solved also for the second value of θ^4. This will be found too low by about 12 per cent., the error decreasing slightly as p increases. The value is corrected by including the θ^{12} term in the equation. By extending the series further, we may calculate as many of the higher whirling speeds or higher frequencies as may be required.

5. *Shaft Carrying Concentrated Masses.*

If the shaft is uniform and of negligible mass but carries at intervals masses which may be regarded as particles, then in (12) we must put

$$\left.\begin{aligned} &\phi(x) = 1, \text{ everywhere ;} \\ &f(x) = 0 \text{ except for } x = x_i,\ i = 1, 2, \ldots, k ; \\ \text{and} \quad &\lim_{\epsilon \to 0} \int_{x_i-\epsilon}^{x_i+\epsilon} f(x)\, dx = \mu_i, \end{aligned}\right\} \qquad (25)$$

where, if M_i is the attached mass,

$$\mu_i = \frac{M_i}{\rho A l}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

Then the required functions have the values :

$$\begin{aligned} f_2(x) = {} & x - \frac{p^2 x^3}{\lfloor 3} + p_4 \frac{x^5}{\lfloor 5} - \text{etc.} \\ & + \theta^4 \Big[S^4 x f(x) - p^2 \Big\{ S^6 x f(x) + S^4 \frac{x^3}{\lfloor 3} f(x) \Big\} \\ & \quad + p^4 \Big\{ S^8 x f(x) + S^6 \frac{x^3}{\lfloor 3} f(x) + S^4 \frac{x^5}{\lfloor 5} f(x) \Big\} \\ & \quad - p^6 \Big\{ S^{10} x f(x) + S^8 \frac{x^3}{\lfloor 3} f(x) + S^6 \frac{x^5}{\lfloor 5} f(x) \\ & \qquad + S^4 \frac{x^7}{\lfloor 7} f(x) \Big\} + \text{etc.} \Big] \\ & + \theta^8 \Big[S^4 f(x)\, S^4 x f(x) - p^2 \Big\{ S^6 f(x)\, S^4 x f(x) \\ & \qquad + S^4 f(x)\, S^6 x f(x) + S^4 f(x)\, S^4 \frac{x^3}{\lfloor 3} f(x) \Big\} + \text{etc.} \Big] \\ & - \text{etc.} \end{aligned}$$

$$\begin{aligned} f_4(x) = {} & \frac{x^3}{\lfloor 3} - p^2 \frac{x^5}{\lfloor 5} + p^4 \frac{x^7}{\lfloor 7} - \text{etc.} \\ & + \theta^4 \Big[S^4 \frac{x^3}{\lfloor 3} f(x) - p^2 \Big\{ S^6 \frac{x^3}{\lfloor 3} f(x) + S^4 \frac{x^5}{\lfloor 5} f(x) \Big\} \\ & \quad + p^4 \Big\{ S^8 \frac{x^3}{\lfloor 3} f(x) + S^6 \frac{x^5}{\lfloor 5} f(x) + S^4 \frac{x^7}{\lfloor 7} f(x) \Big\} \\ & \quad - \text{etc.} \Big] \\ & + \theta^8 \Big[S^4 f(x)\, S^4 \frac{x^3}{\lfloor 3} f(x) - p^2 \Big\{ S^6 f(x)\, S^4 \frac{x^3}{\lfloor 3} f(x) \\ & \qquad + S^4 f(x)\, S^6 \frac{x^3}{3} f(x) + S^4 f(x)\, S^4 \frac{x^5}{5} f(x) \Big\} + \text{etc.} \Big] \\ & - \text{etc.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28) \end{aligned}$$

Now it is easily verified that

$$\mathrm{S}^n \frac{x^r}{\lfloor r} f(x) = \left| \begin{array}{c|c|c} \underline{x<a_1.} & \underline{x>a_1.} & \underline{x>a_2.} \\ 0 & +\mu_1 \frac{(x-a_1)^r}{\lfloor r} \frac{(x-a_1)^{n-1}}{\lfloor n-1} & +\mu_2 \frac{(x-a_2)^r}{\lfloor r} \frac{(x-a_2)^{n-1}}{\lfloor n-1} \end{array} \right| + \text{etc.}$$

$$\mathrm{S}^m f(x)\, \mathrm{S}^n \frac{x^r}{\lfloor r} f(x) = \left| \begin{array}{c|c|c} \underline{x<a_2.} & \underline{x>a_2.} & \underline{x>a_3.} \\ 0 & +\mu_1\mu_2 \frac{(a_2-a_1)^{n-1}}{\lfloor n-1} \frac{(x-a_2)^{m-1}}{\lfloor m-1} & +\mu_1\mu_3 \frac{(a_3-a_1)^{n-1}}{\lfloor n-1} \frac{(x-a_3)^{m-1}}{\lfloor m-1} + \text{etc.} \\ & & +\mu_2\mu_3 \frac{(a_3-a_2)^{n-1}}{\lfloor n-1} \frac{(x-a_3)^{m-1}}{\lfloor m-1} + \text{etc.} \\ & & + \text{etc.} \end{array} \right| \quad . \quad . \quad . \quad (29)$$

Hence, writing $1-a_i = b_i$

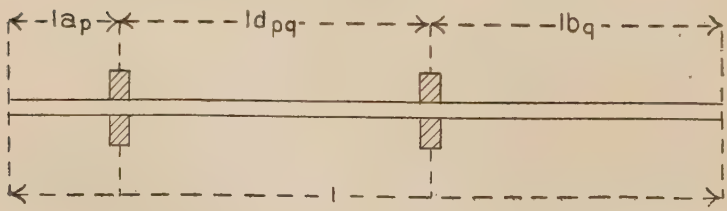
and $1-a_p-b_q = d_{pq}$, (fig. 2),

we have

$$\left. \begin{aligned} \mathrm{S}_1{}^n \frac{x^r}{\lfloor r} f(x) &= \sum_{i=1}^{i=k} \mu_i \frac{a_i{}^r}{\lfloor r} \frac{b_i{}^{n-1}}{\lfloor n-1}, \\ \mathrm{S}_1{}^m f(x)\, \mathrm{S} \frac{x^r}{\lfloor r} f(x) &= \sum_{p,\,q=1}^{k} \mu_p\mu_q \frac{a_p{}^r}{\lfloor r} \frac{d_{pq}{}^{n-1}}{\lfloor n-1} \frac{b_q{}^{m-1}}{\lfloor m-1}, \end{aligned} \right\} \quad (30)$$

where, in the last summation, each pair of masses is taken once only and $p<q$.

Fig. 2.



These give the following values of the functions in which, since the scope of each summation is obvious, the suffixes have been dropped :

$$f_2''(1) = -p^2 + p^4 \frac{1}{\lfloor\underline{3}} - p^6 \frac{1}{\lfloor\underline{5}} + \text{etc.}$$

$$+ \theta^4 \Big[\Sigma\mu ab - p^2 \Sigma\mu \Big(a \frac{b^3}{\lfloor\underline{3}} + \frac{a^3}{\lfloor\underline{3}} b \Big)$$

$$+ p^4 \Sigma\mu \Big(a \frac{b^5}{\lfloor\underline{5}} + \frac{a^3}{\lfloor\underline{3}} \frac{b^3}{\lfloor\underline{3}} + \frac{a^5}{\lfloor\underline{5}} b \Big)$$

$$- p^6 \Sigma\mu \Big(a \frac{b^7}{\lfloor\underline{7}} + \frac{a^3}{\lfloor\underline{3}} \frac{b^5}{\lfloor\underline{5}} + \frac{a^5}{\lfloor\underline{5}} \frac{b^3}{\lfloor\underline{3}} + \frac{a^7}{\lfloor\underline{7}} b \Big) + \text{etc.} \Big]$$

$$+ \theta^8 \Big[\Sigma\mu\mu a \frac{d^3}{\lfloor\underline{3}} b - p^2 \Sigma\mu\mu \Big(a \frac{d^3}{\lfloor\underline{3}} \frac{b^3}{\lfloor\underline{3}} + a \frac{d^5}{\lfloor\underline{5}} b + \frac{a^3}{\lfloor\underline{3}} \frac{d^3}{\lfloor\underline{3}} b \Big)$$

$$+ p^4 \Sigma\mu\mu \Big(a \frac{d^3}{\lfloor\underline{3}} \frac{b^5}{\lfloor\underline{5}} + a \frac{d^5}{\lfloor\underline{5}} \frac{b^3}{\lfloor\underline{3}} + \frac{a^3}{\lfloor\underline{3}} \frac{d^3}{\lfloor\underline{3}} \frac{b^3}{\lfloor\underline{3}} + a \frac{d^7}{\lfloor\underline{7}} b$$

$$+ \frac{a^3}{\lfloor\underline{3}} \frac{d^5}{\lfloor\underline{5}} b + \frac{a^5}{\lfloor\underline{5}} \frac{d^3}{\lfloor\underline{3}} b \Big) - \text{etc.} \Big],$$

$$f_2(1) = 1 - p^2 \frac{1}{\lfloor\underline{3}} + p^4 \frac{1}{\lfloor\underline{5}} - \text{etc.}$$

$$+ \theta^4 \Big[\Sigma\mu a \frac{b^3}{\lfloor\underline{3}} - p^2 \Sigma\mu \Big(a \frac{b^5}{\lfloor\underline{5}} + \frac{a^3}{3} \frac{b^3}{\lfloor\underline{3}} \Big)$$

$$+ p^4 \Sigma\mu \Big(a \frac{b^7}{\lfloor\underline{7}} + \frac{a^3}{\lfloor\underline{3}} \frac{b^5}{\lfloor\underline{5}} + \frac{a^5}{\lfloor\underline{5}} \frac{b^3}{\lfloor\underline{3}} \Big)$$

$$- p^6 \Sigma\mu \Big(a \frac{b^9}{\lfloor\underline{9}} + \frac{a^3}{\lfloor\underline{3}} \frac{b^7}{\lfloor\underline{7}} + \frac{a^5}{\lfloor\underline{5}} \frac{b^5}{\lfloor\underline{5}} + \frac{a^7}{\lfloor\underline{7}} \frac{b^3}{\lfloor\underline{3}} \Big) + \text{etc.} \Big]$$

$$+ \theta^8 \Big[\Sigma\mu\mu a \frac{d^3}{\lfloor\underline{3}} \frac{b^3}{\lfloor\underline{3}}$$

$$- p^2 \Sigma\mu\mu \Big(a \frac{d^3}{\lfloor\underline{3}} \frac{b^5}{\lfloor\underline{5}} + a \frac{d^5}{\lfloor\underline{5}} \frac{b^3}{\lfloor\underline{3}} + \frac{a^3}{\lfloor\underline{3}} \frac{d^3}{\lfloor\underline{3}} \frac{b^3}{\lfloor\underline{3}} \Big) + \text{etc.} \Big].$$

$$f_4''(1) = 1 - p^2\frac{1}{\lfloor\underline{3}} + p^4\frac{1}{\lfloor\underline{5}} - \text{etc.}$$
$$+\theta^4\Big[\Sigma\mu\frac{a^3}{\lfloor\underline{3}}b - p^2\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^3}{\lfloor\underline{3}} + \frac{a^5}{\lfloor\underline{5}}b\Big)$$
$$+p^4\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^5}{\lfloor\underline{5}}\frac{b^3}{\lfloor\underline{3}} + \frac{a^7}{\lfloor\underline{7}}b\Big)$$
$$-p^6\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^7}{\lfloor\underline{7}} + \frac{a^5}{\lfloor\underline{5}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^7}{\lfloor\underline{7}}\frac{b^3}{\lfloor\underline{3}} + \frac{a^9}{\lfloor\underline{9}}b\Big) + \text{etc.}\Big]$$
$$+\theta^8\Big[\Sigma\mu\mu\frac{a^3}{\lfloor\underline{3}}\frac{d^3}{\lfloor\underline{3}}b$$
$$-p^2\Sigma\mu\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{d^3}{\lfloor\underline{3}}\frac{b^3}{\lfloor\underline{3}} + \frac{a^3}{\lfloor\underline{3}}\frac{d^5}{\lfloor\underline{5}}b + \frac{a^5}{\lfloor\underline{5}}\frac{d^3}{\lfloor\underline{3}}b\Big) + \text{etc.}\Big],$$

$$f_4(1) = \frac{1}{\lfloor\underline{3}} - p^2\frac{1}{\lfloor\underline{5}} + p^4\frac{1}{\lfloor\underline{7}} - \text{etc.}$$
$$+\theta^4\Big[\Sigma\mu\frac{a^3}{\lfloor\underline{3}}\frac{b^3}{\lfloor\underline{3}} - p^2\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^5}{\lfloor\underline{5}}\frac{b^3}{\lfloor\underline{3}}\Big)$$
$$+p^4\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^7}{\lfloor\underline{7}} + \frac{a^5}{\lfloor\underline{5}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^7}{\lfloor\underline{7}}\frac{b^3}{\lfloor\underline{3}}\Big)$$
$$-p^6\Sigma\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{b^9}{\lfloor\underline{9}} + \frac{a^5}{\lfloor\underline{5}}\frac{b^7}{\lfloor\underline{7}} + \frac{a^7}{\lfloor\underline{7}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^9}{\lfloor\underline{9}}\frac{b^3}{\lfloor\underline{3}}\Big) + \text{etc.}\Big]$$
$$+\theta^8\Big[\Sigma\mu\mu\frac{a^3}{\lfloor\underline{3}}\frac{d^3}{\lfloor\underline{3}}\frac{b^3}{\lfloor\underline{3}}$$
$$-p^2\Sigma\mu\mu\Big(\frac{a^3}{\lfloor\underline{3}}\frac{d^3}{\lfloor\underline{3}}\frac{b^5}{\lfloor\underline{5}} + \frac{a^3}{\lfloor\underline{3}}\frac{d^5}{\lfloor\underline{5}}\frac{b^3}{\lfloor\underline{3}} + \frac{a^5}{\lfloor\underline{5}}\frac{d^3}{\lfloor\underline{3}}\frac{b^3}{\lfloor\underline{3}}\Big) + \text{etc.}\Big].$$
. . . (31)

From these formulæ and equation (21), which applies equally in the present problem, an equation of the form

$$A\theta^4 = B + C\theta^8$$

may be obtained for each value of p. The neglect of the θ^8 term must lead, exactly as was shown for the shaft without end-thrust *, to a formula equivalent, in the case of

* *Loc. cit.* p. 1.

whirling, to Dunkerley's *, while the θ^8 term gives a correction to the first approximation and allows the error in Dunkerley's rule to be estimated.

The calculation has been made for two, three, and five equal masses, equally spaced. Of the details of this work it is sufficient to mention :

(1) That the terms independent of θ in the above series are expressible in terms of $\sin p$ and may be calculated readily.

(2) That in the coefficients of θ^4 and θ^8 no more terms are needed than are shown above.

(3) That for symmetrically spaced loads, $f_2''(1), f_4(1)$ are identical, while in the various summations many of the terms become equal in pairs.

Even with these simplifications, the calculation is laborious when values of p^2 up to 9 are considered. When, however, as will generally be the case in practice, p is small, very few terms are needed for a reasonably accurate result.

The values of $\mu\theta^4$ given by the first approximation (*i. e.* by Dunkerley's rule) are given in Table IV. ; the corrected values obtained by including the θ^8 term are shown in Table V. In Table VI. are given the errors consequent on the use of Dunkerley's rule in each case The results are given for four different values of the end-thrust and four of the tension, in addition to the zero value. The corrections for a uniform shaft are added for comparison.

TABLE IV.

Values of $\mu\theta^4$ given by Dunkerley's Rule.

	p^2.	2 masses.	3 masses.	5 masses.
Tension	−8	41·90	31·07	20·64
	−4	39·05	28·91	19·24
	−2	36·18	26·87	17·84
	−1	33·29	24·74	16·43
	0	30·38	22·59	15·00
Thrust.....	1	27·44	20·42	13·53
	2	24·49	18·23	12·14
	4	18·49	13·79	9·23
	8	6·10	4·62	3·07

* Phil. Trans. A, clxxxv. (1894).

TABLE V.

Corrected Values of $\mu\theta^4$

	p^2.	2 masses.	3 masses.	5 masses.
Tension	−8	45·62	34·38	23·00
	−4	42·35	31·84	21·28
	−2	38·92	29·33	19·57
	−1	35·67	26·82	17·89
	0	32·38	24·37	16·32
Thrust	1	28·97	21·90	14·60
	2	25·74	19·41	12·97
	4	19 31	14·52	9·75
	8	6·21	4·72	3·14

TABLE VI

Errors in ω as given by Dunkerley's Rule.

	p^2.	2 masses. per cent.	3 masses. per cent.	5 masses. per cent.	Uniform Shaft. per cent.
Tension	−8	4·1	4·8	5·1	5·1
	−4	3·9	4·5	4·8	4·8
	−2	3·5	4·2	4·4	4·4
	−1	3·3	3·9	4·1	4·1
	0	3·1	3·6	3·8	3·8
Thrust	1	2·9	3·2	3·5	3·5
	2	2·5	3·1	3·2	3·2
	4	2·1	2·5	2·6	2·6
	8	0·9	1·0	1·0	1·0

All the errors have the same sign, the value of ω given being consistently too low.

As the number of loads increases, the value of the error rapidly tends to the limiting value which it has for the uniform shaft. This limiting value decreases as the thrust increases.

Thus the error in Dunkerley's rule is greater for a shaft with tension and less for one with thrust than for a shaft without longitudinal stress. For moderate values of the stress the error is from 3·5 per cent. to 4 per cent. and is one of deficit.

I am indebted to Prof. L. N. G. Filon for valuable criticism and suggestions.

LVIII. *New Series in the Secondary Hydrogen Spectrum.* By W. E. Curtis, *D.Sc., A.R.C.S., Reader in Physics in the University of London, King's College* *.

IN view of the progress which is being made towards the solution of the problem of the analysis of the secondary hydrogen spectrum, it may be worth while to record several new series which I have recently found in this spectrum. They are only single branches, but if associated branches exist the particulars here given may assist workers in this field to discover them. In any case the spectrum is at present being studied under such widely varying conditions that evidence as to the genuiness or otherwise of the alleged series should not be long in appearing.

The first, denoted K, came to light during the examination of some work by Kimura and Nakamura † dealing with the influence of the electrodeless discharge on the secondary spectrum of hydrogen. They have given a list of some twenty lines which are enhanced under these conditions, and have pointed out several possible regularities amongst them. Of these, the only one which repaid further investigation was a sequence of four lines showing very small and almost constant second differences of wave-number. Reference to Merton and Barratt's tables gave two more members of the series on one side and a possible one on the other, making seven in all. The second differences are not quite constant, but increase so regularly that the reality of the series can hardly be doubted, especially when the intensity distribution and general properties of the lines are also taken into consideration.

Search was then made ‡, using a graphical method, for other possible series in the same region and having first and second differences of the same order. Two were found, denoted G and H below, comprising six and five lines respectively. It was then noticed that four successive lines of G were included in Kimura and Nakamura's list; this circumstance, together with evidence derived from the properties, lends considerable support to the proposed arrangement. The credentials of H are hardly so good. There are only five lines, the middle one alone being recorded as strengthened by the electrodeless discharge,

* Communicated by Prof. O. W. Richardson, F.R.S.

† Japanese Journ. Phys. vol. i. p. 86 (1923).

‡ By my wife.

although four of them are listed by Merton and Barratt as enhanced by a condensed discharge. The sensible constancy of the second differences cannot be regarded as decisive evidence, in view of the shortness of the series, but as a provisional arrangement it may be worthy of notice in future investigations.

In the table given below the columns headed L.P., H.P., C.D., and He are taken from Merton and Barratt's tables, and record the characteristics of the line as regards low pressure, high pressure, condensed discharge, and helium effect.

In column S the two lines marked — are noted by Sandeman * as being much weakened in a discharge at atmospheric pressure as compared with an ordinary vacuum tube discharge.

Column R records the behaviour in Richardson and Tanaka's three types of discharge †.

Column K indicates the lines strengthened in the electrodeless discharge, as recorded by Kimura and Nakamura.

Column T gives the behaviour at a temperature of −252° C., according to the observations of McLennan and Shrum ‡.

Z indicates that a Zeeman effect has been observed. The present region is just outside the range of Dufour's results which are listed in Merton and Barratt, but is partially covered by an investigation of Croze §.

In cases where the line has already been allocated to a series, particulars are given in column X. The line marked F II is one of those added to Fulcher's second band by Allen ||. The remainder have been used by Richardson in various bands which he has recently published.

Series K may be regarded as well established, both on account of the very regular wave-number differences and of the similarity in behaviour of the lines with respect to temperature and the condensed discharge. But it is doubtful whether the first line, 16980, is really associated with the others, although the wave-number fits very well.

17426 figures as R(2) in Richardson and Tanaka's series no. 201¶, where however it is much too strong, and the authors suggest that there is a strong line superposed on

* Roy. Soc. Proc. A, cviii. p. 607 (1925).

† Roy. Soc. Proc. A, cvi. p. 640 (1924). This information was kindly supplied to me by Prof. Richardson.

‡ Trans. Roy. Soc. Canada, xviii. p. 177 (1924).

§ *Ann. de Phys.* i. p. 63 (1914). No observations below 5760 A.

|| Roy. Soc. Proc. A, cvi. p. 69 (1924).

¶ Roy. Soc. Proc. A, cvi. p. 663 (1924)

Series K.

λ_{air}	Int.	$\nu_{vac.}$	H.P.	S.	L.P.	R.	C.D.	K.	T.	He	Z.	X.	1st diff.	2nd diff.	3rd diff.
5887·35	0	16980·87	+	...	−	...	−	..	...	+			149·49		
35·98	9	17130·36	...	...	+ +	...	+ +	+	+	...	Z	...		0·96	
5785·81	7	278·89	...	..	+ +	I+	+	+	+ +	...	Z	...	148·53		0·21
36·88	8	426·25	...	−	...	...	+	+	+ +	...	...	201 R	147·36	1·17	
5689·19	7	572·31	+	...	...	I−, II−	+ +	+	−	0	...	...	146·06	1·30	0·13
42·78	3	716·87	...	...	...	II−	+ +	...	...	+	...	81 R	144·56	1·50	0·20
5597·63	4	859·75	...	...	+ +	...	+	...	+				142·88	1·68	0·18

Series G.

5922·01	0	16881·52											144·30		
*5871·81	4	17025·82	...	...	+ +	...	+ +	...	...	...	Z	157 Q		1·00	
22·80	5	169·12	...	...	+ +	...	+ +	+	+ +	..	Z	186 R	143·30		
*5774·98	7	311·28	...	...	+ +	...	+ +	+	+	...	Z	...		1·14	
28·54	7	451·61	+	−	...	II−	+ +	+	+	0	...	201 R	142·16		
5683·05	2	591·33	...	...	...	...	+ +	+	...	...	...	F II		1·83	
													140·33		
														1·01	
													139·72		

Series H.

5989·22	5	16692·04	+ +	..	...	I−	+						149·61		
36·02	4	841·65	...	...	...	...	...	...	...	0	...	..		0·35	
5883·88	6	990·91	+ +	...	...	II−, III−	+ +	+	...	...	...	...	149·26		
32·89	5	17139·43	...	...	...	...	+ +	...	...	...	...	...		0·74	
5783·01	2	287·25	...	...	...	...	+ +	...	...	+			148·52		
														0·70	
													147·82		

* Unresolved doublets (M. & B.).

the real R(2). This is supported by Sandeman's observation that in the high-pressure discharge this line is much weakened in comparison with the remainder of the series (except 17451·61, *q. v.* below). It is thus probable that the K component of this line is of a low-pressure character, like the two preceding lines in the series.

17572 is exceptional in its pressure and temperature effects and may very well also be a blend.

17716 is claimed by Richardson and Tanaka * as 81 R(7), but is a good deal stronger than their series seems to require and in their opinion may be "double, with constituents which are differentially affected by He."

Series G consists of only six lines, and the second differences show a slight irregularity which may be attributed to the observed duplicity of two of the lines. The properties are in good agreement except for 17451, but this is evidently due to the superposition of Richardson's 201 R(5), which being a high-pressure line masks the low-pressure character of the G line. This comes out clearly in Sandeman's observation at atmospheric pressure, where the intensity of this blend drops from 7 (M. & B., low pressure) to 3, bringing it into line with the rest of 201 R, evidently because the G constituent is suppressed. We conclude that the latter must be a low-pressure line, and it therefore agrees in this respect with the other three strong members of this series.

17025 coincides with Richardson's 157 Q(4)† and is noted as double by Merton and Barratt. It is difficult to estimate what intensity it should have in 157 Q, but since it is double it is permissible to claim one of the components for G.

17169 figures as 186 R(2) ‡, where again the expected intensity is uncertain. But since 186 R has only five lines and less regular differences than G, the latter would appear to have at least as good a claim to it.

17591 has already been allocated to the second Fulcher band §, but seems a little too strong there. Its inclusion here is justified by its appearance in Kimura and Nakamura's list, where no other Fulcher line is to be found. But it is just possible that 17588 should be included instead.

Series H is somewhat problematical, but the differences are sufficiently regular to secure it some consideration. Also, four of its five lines are strengthened by the condensed discharge. None of them appear to have been already allocated to other series.

* Roy. Soc. Proc. A, cvii. p. 617 (1925).
† Roy. Soc. Proc. A, cix. p. 240 (1925).
‡ *Id.* p. 239.
§ See Curtis, Roy. Soc. Proc. A, cvii. p. 573 (1925).

It is worthy of note that of the 18 lines, mostly strong ones, considered here, only one, 17859, is recorded * as showing a Stark effect, although numerous other lines in this region (some 30 in all) are affected.

Five show a Zeeman effect, but our general acquaintance with the nature of this effect in band spectra has not yet progressed to the point where it is capable of providing definite evidence for or against the proposed arrangement. It may be observed, however, that band lines are susceptible to the Zeeman effect, which is sometimes of the "normal" order of magnitude and is of the same general character for lines belonging to the same branch.

It has not been possible to find any numerical relations between the three series, although their first and second differences are closely similar. K appears to be definitely of R type, but G and H might be either P or R branches. Search for associated branches on either side of this region has not led to any result. It is not likely that a Q branch exists, since the smallness of the second differences would give rise to a very small spacing in such a branch, and since also it should be intense there ought to be no difficulty in detecting it.

The moment of inertia of the molecule concerned in the emission of these bands is about $3{\cdot}7 \times 10^{-41}$ gm. cm.^{2} and the change in its value due to the emission is hardly appreciable, being less than 1 per cent. This is unusual, in fact no other case is known in which the initial and final moments of inertia are so nearly equal. But since the emission process sometimes increases (band degraded towards the violet) and sometimes decreases (band degraded towards the red) the moment of inertia of the molecule, it is to be expected that cases may occasionally occur in which the change is practically nil.

Later Note.—I have recently availed myself of an opportunity (for which I have to thank Prof. Richardson) of examining one of Prof. Merton's plates of the secondary spectrum on which was also a comparison spectrum showing the "helium effect". Estimates were made of the intensities in each case, with the following results. The normal intensity is given first, *e. g.* 10, 2 means that the normal intensity 10 becomes 2 in presence of helium.

* Kiuti, Japanese Journ. Phys. vol. i. p. 29 (1922).

No.	K Series.	G Series.	H Series.
1	0, 0?	0, 0	5, 1
2	10, 2	6, —	4, 4
3	10, 2	7, 2+	6, 4
4	9, 3	8+, 2+	6, 1
5	7, 9	7−, 8	1, 2
6	3, 3	1, —	
7	4, —		

The striking similarity in the behaviour of K and G is strong evidence of the reality of both series. The distribution of the effect in the series is very like that in the Fulcher quintet at 6018 (the only one showing it clearly) where the fourth and fifth members are greatly strengthened by helium relative to the remainder (seen from the plate but not apparent from the tables, which do not indicate, either, the helium effects given above).

The observations do not support H in the same way, but this has throughout been regarded as a provisional arrangement, which would require confirmation before it could be accepted.

In addition, it was noted that K 6 is almost certainly double, since in helium it is appreciably displaced, suggesting that one component is suppressed. This supplements the evidence of duplicity previously put forward, viz. its allocation to Prof. Richardson's series 81 R.

In conclusion it may be observed that the object in view has been to give all the evidence concerning every line, even though it might not directly bear on the question as to whether the lines are associated. Since some of it is incomplete (*e. g.* Sandeman only examined one K line) and some difficult to interpret, the case for the alleged series must be regarded as resting mainly on the numerical relationships between the wave-numbers and the similarity of the electrical conditions favourable to the production of the lines.

LIX. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 560.]

November 4th, 1925.—Dr. J. W. Evans, C.B.E., F.R.S., President, in the Chair.

THE following communications were read:—

1. 'Preliminary Notes on the Geology of the Eastern Parts of Central Spitsbergen: with especial reference to the Problem of the Hecla Hook Formation.' By Noel Ewart Odell, Assoc.R.S.M., F.G.S.

The region dealt with is that of New Friesland and Garwoodland, traversed by the inland sledging parties of the Oxford

University (Scientific) Expedition to Spitsbergen, 1921, and also by the Merton College (Oxford) Arctic Expedition, 1923.

Approximately, the area amounts to 2000 square miles, but only a relatively small portion of this could be actually examined. It consists of a mountainous tract much of which is submerged under 'highland ice' and glaciers, and is therefore lacking in direct rock-evidence. But through this ice-covering break many 'nunatakkr', and on the west of the region a high range of mountains—the Chydenius Range—of which Mount Newton (5445 feet) is claimed to be the culminating point of Spitsbergen.

The rocks encountered include representatives of the Metamorphic Basement Complex, the Hecla Hook formation (which is intimately associated with that complex), the Carboniferous System, and intrusive acid and basic igneous facies.

The Metamorphic Complex and the Hecla Hook formation have long proved the chief enigma of Spitsbergen geology. The former, often designated the 'Urgebirge,' was long considered to be Archæan, and the latter (owing to complete lack of fossils throughout its great thickness) could not be dated. The relations of these two formations are rendered obscure by the intense folding and dislocation which they have suffered in most accessible areas.

There is an occurrence analogous to the Hecla Hook formation of Spitsbergen in Bear Island, situated half way between Spitsbergen and Norway, and this has been shown to be Ordovician in greater part, with a fauna of distinct American affinities.

The author found evidence in the extreme east of Spitsbergen, so much less highly disturbed than the west, of a lithological series of Hecla Hook rocks comparable with those described from Bear Island, although, with one possible exception, no unequivocal evidence of fossils could be obtained. Moreover, such sequences as were observed corresponded in general to those of Bear Island, although it would appear that in Spitsbergen there is exposed, in addition, a Lower Series of slates and massive quartzites of unknown thickness.

The whole formation in downward succession is as follows:—

Upper Series.

(7) Cherty conglomerate.
(6) Black and white chert-horizon.
(5) Pale and dark dolomites and limestones of great thickness, often veined with calcite and dolomite, including an 'intra-dolomite conglomerate' present in Bear Island, and a fossil horizon of 'oolitoid' rock or 'ryssö-dolomite'.
(4) Red shales, with thin quartzites and quartzose slates.

Lower Series.

(3) Marbles and dark dolomitic limestones.
(2) Dark shales, hard buff-coloured and blue slates weathering green, often spotted, and interbedded with pink quartzite.
(1) Purple massive quartzite, Pink massive quartzite, Yellow massive quartzite } about 1000 feet exposed.

The above succession must be considered as tentative only, since

the interrelationships of the members of the Lower Series in particular were very obscure, owing to dislocation and ice-covering. If, as is probable, No. 3 in the succession corresponds with Prof. O. Holtedahl's 'Ozarkian Stage' in the Bear Island sequence, then the lowest members are of Cambrian age.

A great north-and-south fault through the centre of the region is shown on A. G. Nathorst's map of 1910, but the existence of this was not confirmed. Instead, the line marks a zone of great stress, and the Hecla Hook formation here suffers its greatest metamorphosis: interbedded with the highly altered sediments in this zone are intrusive rocks of granitoid and more basic affinities, the basic appearing the earlier.

No evidence was found of rocks earlier in age than the Hecla Hook Series, and an Archæan formation must be presumed absent.

The greatest acid intrusions are those of the pink and grey granites in the Mount Newton and Mount Chernishev massif. Evidence was obtained of the pre-Carboniferous (and presumably pre-Devonian) age of both these granites. They would appear to have been intruded at the time of the Caledonian folding, and though towards its close, yet prior to the earliest Devonian sedimentation.

Except in the south on the Nordenskiöld Glacier, where an erratic block of conglomerate was found, the Devonian strata are entirely absent from this region, having been eroded from the interfolded Hecla Hook sediments and granites before the transgression of the Upper Carboniferous sea. The Culm also is absent.

The Carboniferous, with its extensive dolerite-sills of Cretaceous age, has been much involved in the block-movements that resulted in the formation of the graben of Hinlopen Strait in Tertiary times, New Friesland correspondingly within that era being re-elevated as a horst.

The existing general geological maps of Spitsbergen, mostly based upon that of Nathorst (1910), indicate too great an areal extent of the Carboniferous. It was found to be confined more to the coast of Hinlopen Strait, from Cape Fanshawe as far south as Bismarck Strait. Moreover, Triassic deposits were not seen north of the latter, as opposed to their usual indication on the maps.

The Hecla Hook formation, with its highly metamorphosed components and associated intrusive suites, comprises, with the above-mentioned exceptions of Carboniferous and Triassic rocks, the whole region lying between Wijde Bay on the west and Hinlopen Strait on the east. It extends southwards to the neighbourhood of Sassen Bay on Ice Fiord; and it may be made to embrace the whole area variously indicated as 'Archæan' or 'Urgebirge' on the existing maps.

2. 'The Geology of North-East Land (Spitsbergen).' By Kenneth Stuart Sandford, M.A., D.Ph., F.G.S.

This paper is chiefly the result of exploration by the Oxford University Arctic Expedition of 1924. North-East Land is

separated by a narrow strait from the main island of Spitsbergen, and is about 8000 square miles in area. A great part of the coast and the whole of the interior are completely hidden by ice, which forms a dome rising to about 2400 feet. The paper attempts to show the geological history as deduced from such of the barren, ice-free outcrops as have been visited, and from a study of moraines.

North-East Land may be divided into two parts:—

Northern Area, consisting of Older Palæozoic rocks, granite, and gneiss: discussion arises as to the age of the last two, and the evidence, although not yet conclusive, in the author's opinion points to their being younger than the ancient sedimentary rocks: a pink granite penetrates the grey granite and gneiss, and has been found extensively developed in the southern part of this 'northern oldland.' An important discovery in 1924 was the south-eastern corner of the 'northern oldland' pink granite, in the middle of the east coast, which previously had been known only as an unbroken and precipitous ice-front over 100 miles long. The older Palæozoic—Hecla Hook formation—probably comprises the Cambrian to Silurian (from external evidence): it consists of unfossiliferous shales, quartzite, and dolerites to a very great thickness; there appears to be a general sequence over a wide area. Most of Spitsbergen was intensely affected by Caledonian folding and thrusting: the author has found in North-East Land the margin of this chain; the north-eastern part appears to be unfolded, while a narrow arc of intense disturbance affected part of the west coast, sending out ripples of rapidly decreasing magnitude. In Devonian times a vast thickness of deposits was formed in and over the Caledonian mountains: in North-East Land, however, only a trace (morainic material) of Devonian deposits has been found.

The Archipelago was next broken by block movement, and by the formation of broad graben and horsts: North-East Land appears to have been implicated. Of the Lower Carboniferous only uncertain traces have been found in moraines: the Middle Carboniferous is not exposed.

Southern Area, delimited from the northern by an east-and-west fjord. This is an area of undisturbed Upper Carboniferous and Permo-Carboniferous clays and cherts, to a visible thickness of more than 1000 feet: the fauna belongs to the Russian Province. A small area of Permian is known on the south-west coast, and is followed southwards by a few hundred feet of Trias. Close by, an island has been shown by Baron G. J. de Geer to consist of thin Jurassic beds (with coal) overlain by basalt (associated with dolerite; see below) and thin Cretaceous beds. The Jurassic sea extended south-south-westwards and eastwards to Franz Josef Land. North-East Land appears to have been implicated in extensive Lower Cretaceous base-levelling.

At this time enormous quantities of dolerite ascended along vertical fissures of definite trend from which originated basalt-flows, and dolerite-sills of great length and uniform thickness

(one 150 feet thick extending at least 40 miles). No Tertiary deposits have been found in North-East Land, and probably do not exist: they are well developed on the south-west (in Spitsbergen itself), where also there was strong folding in late Tertiary times along the Caledonian lines: North-East Land was unaffected.

The folding was followed by extensive fjord formation: on the west side of North-East Land the author finds especial significance in the coincidence of one set of fjords with the dolerite-fissures and a second set, destitute of dolerite, crossing them—at the crossing-point the maximum intrusion of dolerite occurred. The lines of weakness are, therefore, probably at least of Lower Cretaceous age. The Quaternary and recent history of North-East Land is not discussed in this paper.

The history of the island has been one of quiescence and immunity from folding, in an area of shallow seas. It has been affected by vertical movements, also by acid intrusions (Palæozoic) and by basic intrusions (Cretaceous).

LX. *Intelligence and Miscellaneous Articles.*

THE WATER-SPARK ABSORPTION SPECTRUM OF IRON.

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a recent number of the Phil. Mag. (vol. i. p. 433, 1926) we find a very interesting article by Mr. N. K. Sur, "On the Water-Spark Absorption Spectrum of Iron." The author mentions the names of Wilsing, Hale, Konen, Victor Henri, Hulert, Angerer and Joos in connexion with this; and it would appear from this that he is not aware of our work "Spèctres d'étincelle dans l'eau" (*Le Journal de Physique et le Radium*, t. iii. d. 309, 1922). We may perhaps be permitted to remind him that this work embraces a detailed study of the water-spark absorption spectrum of Iron with a Table of the lines of absorption, which, commencing at a lower point and proceeding further than that of Mr. Sur, shows a considerably greater number of lines, and in the region common to both the lists practically coincide.

Yours faithfully,

LÉON BLOCH,
EUGÈNE BLOCH.

Paris, February 13, 1926.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]